ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF THE EFFECT OF PHOTOSTABILIZERS ON MECHANICAL PROPERTIES AND SURFACE ANALYSIS OF COTTON FIBER REINFORCED LDPE COMPOSITES

M.Sc. THESIS

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Department of Polymer Science and Technology
Polymer Science and Technology Department

Thesis Advisor: Prof. Dr. İ.Ersin SERHATLI

MAY, 2015

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FOTO DÜZENLEYİCİLERİN PAMUK LİFİ TAKVİYELİ DÜŞÜK YOĞUNLUKLU POLİETİLEN KOMPOZİT MALZEMELERİN MEKANİK ÖZELLİKLERİNE VE YÜZEY ANALİZİNE ETKİSİNİN İNCELENMESİ

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To my family,

FOREWORD

This study has been carried out in Composite Laboratory in Faculty of Mechanical Engineering and POLMAG Laboratory (Polymeric Materials Research Group), Faculty of Science and Letters, Istanbul Technical University.

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ABBREVIATIONS

PP	**:** Polypropylene
PS	**:** Polystyrene
PET	**:** Polyethylene terephthalate
PVC	**:** Polyvinyl chloride
LDPE	**:** Low density polyethylene
UVA	**:** Ultraviolet absorber
UV	**:** Ultraviolet
IR	**:** Infrared
HALS	**:** Hindered amine light stabilizer
AOx	**:** Antioxidant
CNC	**:** Computer numerical control
FTIR	**:** Fourier transform infrared
DSC	**:** Differential Scanning Calorimetry
CF/LDPE	**:** Cotton fiber/Low density polyethylene
MOE	**:** Modulus of elasticity
TS	**:** Tensile strength
SEM	**:** Scanning electron microscopy
CB-D	**:** Chain breaking donor
CB-A	**:** Chain breaking acceptor
nm	**:** Nanometer
ΔH_m	**:** Heat of fusion
T_g	**:** Melting temperature
a*	**:** Red-green coordinate
b*	**:** Yellow-blue coordinate
L*	**:** Lightness coordinate
ΔE	**:** Discoloration

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THE EFFICACY OF PHOTOSTABILIZRS ON MECHANICAL PROPERTIES AND SURFACE ANALYSIS IF COTTON FIBER REINFORCED LDPE COMPOSITES

SUMMARY

Fiber reinforced composites have gained much acceptance in recent years. Synthetic fibers like glass, carbon and aramid are widely being used in polymer based composites because of their high stiffness and strength properties. However, these fibers have serious disadvantages in terms of their biodegradability, costs, recyclability, energy consumption etc. Although synthetic fibers currently dominate the polymer industry, the use of natural fibers as reinforcing substance in the thermoplastic industry has become more accepted.

Natural fibers are subdivided based on their origins, coming from plants, animals or minerals. Especially wood fiber, which is generally preferred in the composite production, reinforced composites are used in the construction industry for applications such as decking, siding, roofing tiles and window frames[1]. The use of cotton fiber could be an alternative reinforcement in the replacement of wood fiber, especially in the outdoor environment. The natural fiber composites expose outdoors undergo expecially photo-oxidation degradation caused by ultraviolet radiation. This degradation takes place primarily in the lignin substance, which is responsible for the characteristic color changes[2].The presence of 0.7-1.6% lignin content in the cotton structure is advantage for the cotton fiber[3]. Cotton fiber have very promising physical properties as a fiber in plastic/fiber composites but there have been few studies about plastic/cotton fiber composites[4]. Thermal stability, moisture resistance, fungal resistance and ultraviolet exposure (UV) are included in the outdoor durability of composites. UV exposure is one of the important concern about the durability of these composites when exposed to outdoor environment. For example, UV exposure can cause the composites to undergo photo-degradation leading to undersirable effects, including a loss in mechanical properties and surface quality, i.e. surface micro-cracking and color change. To prevent the photodegradation and extend service life of cotton fiber reinforced polyethylene (CF/LDPE) composites, various stabilizers were introduced to eliminate or delay the UV light exposure on the CF/LDPE composites, or dissipate the enegry of molecules in the excited state[1, 5].

In this study, the use of photo-stabilizers such as UV absorbers (UVA), hindered amine light stabilizers (HALS-free radical scavengers) and antioxidants were used to minimize the effect of UV exposure in the cotton fiber reinforced low density polyethylene composites.. Cotton fiber reinforced LDPE (CF/LDPE) composites were manufactured by using a custom made single screw extruder. After the manufacturing process, composite plates were pressed to maintain constant thickness

and flatness. Samples were cut out by using a desktop CNC milling machine for tensile and impact testing. Composite materials were exposed to both Ultraviolet (UV) light exposure for the time periods of up to 240h. To investigate the effect of photostabilizers on mechanical properties of stabilized and unstabilized CF/LDPE composites, tensile testing was applied to the all composites and compared to each other. Tensile strength, modulus of elasticity and strain at break were calculated from the tensile testing. The strain at break of unstabilized composites decreased upon increasing UV exposure. That means the CF/LDPE composites became very brittle after weathering. The largest drop was seen in the unstabilized composites in strain at break which was nearly %. CF/LDPE stabilized with HALS showed the better tensile strength properties than the other stabilized composites after 240h of weathering. UV absorbers also affected positively the mechanical properties. The presence of UVA in the composites reduces the rate of decline of the strain at break. Also the CF/LDPE composites stabilized with UVA prevented the loss in modulus of elasticity after weathering. The using antioxidants(AOx) was also effective for CF/LDPE composites. The modulus of elasticity was increased with increasing exposure time due to the rigidity of composites. Also the impact strength of unstabilized and stabilized composites were determined. Generally, CF/LDPE stabilized with HALS showed the best results on mechanical properties.

Fourier transform infrared (FTIR) spectroscopy has been used to study changes in the surface of chemistry of polyethylene. Carbonyl index of all composites were determined to investigate the degradation of composites upon UV weathering. It was shown that the carbonyl index for unstabilized composite was the highest value after 240h of exposure. For stabilized composites, HALS offers the important protection to the CF/LDPE composites. Also, the CF/LDPE composites stabilized with UVA was more effective than the other stabilized composites.

DSC analysis were determined for obtaining the thermal properties of CF/LDPE composites. The crystallinity values were calculated from DSC curves. The crystallinity values of composites indicates that the chain scission mechanism of polyethylene matrix during photo-degradation. After 120h of weathering, the crystallinity value of unstabilized composites increased due to the chain scission of polyethylene matrix. This value started to decrease after 240h of exposure for unstabilized composites. After 240h of exposure, stabilized composites behaved different from the unstabilized composites. The net change in crystallinity for stabilized composites was not significant. HALS and AOx showed the best results for CF/LDPE composites upon UV weathering.

Color measurement of CF/LDPE composites were determined. The lightness (L*) and chromaticy coordinates (a* and b*) were measured and color change (ΔE*) was calculated. The a* value and b* value of all composites decreased at the same rate during 120h of exposure. The Δb* value of CF/LDPE composite which indicates the yellowing of samples decreased significantly after 240h of exposure. HALS stabilized composites exhibited the most negative change in the Δb* value among the all stabilized composites after 240h of exposure. However, the addition of UV absorbers to the composites resulted in retention of photobleaching. The lightness factor ΔL* increased for all composites after 240h of exposure. After 240h of exposure, most of the stabilized CF/LDPE composites ΔL* values are lower than the unstabilized composite. The CF/LDPE composites stabilized with AOx were most effective for lightness (ΔL*) property. The total discoloration (ΔE*) of CF/LDPE/HALS had the highest ΔE* value along the stabilized composites.

FOTO DÜZENLEYİCİLERİN PAMUK LİFİ TAKVİYELİ DÜŞÜK YOĞUNLUKLU POLİETİLEN KOMPOZİT MALZEMELERİN MEKANİK ÖZELLİKLERİNE VE YÜZEY ANALİZİNE ETKİSİNİN İNCELENMESİ

ÖZET

Lif takviyeli kompozit malzemeler son yıllarda önem kazanmıştır. Cam, karbon ve aramid lifleri gibi sentetik lifler, yüksek sertlik ve dayanım özelliğine sahip olduklarından dolayı polimer katkılı kompozit malzemelerde yaygın biçimde kullanılmaktadır. Fakat sentetik lif takviyeli kompozit malzemeler biobozunurluk, fiyat, geri dönüştürülebilirlik ve enerji tüketimi gibi dezavantajlara sahiptirler. Polimer endüstrisinde sentetik liflerin kullanımı daha fazla olsa da, doğal liflerin takviye elemanı olarak kullanımı oldukça fazladır.

Doğal lifler kökenlerine göre bitki, hayvan ve mineral bazlı olarak ayrılırlar. Özellikle genellikle kompozit üretiminde çok kullanılan odun lifi, takviye elemanı olarak dış kaplama, kiremit ve pencere kasası gibi inşaat endüstrisinde kullanılır. Pamuk lifinin kompozit malzemelerde odun lifine alternatif olarak takviye elemanı olarak kullanılabilir. Doğal lifler 3 ana bileşender oluşurlar: selüloz, hemiselüloz ve lignin. Selükoz doğal liflerin ana bileşenidir. Doğal liflerde dayanıklılık, sertlik ve yapısal kararlılıktan sorumludurlar. Selülozun moleküler yapısı doğal lifin kimyasal ve fiziksel özelliklerini belirler. Hemiselüloz doğal liflerde ikinci ana bileşendir. Dallanmış ve amorf bir yapıya sahip olan hemiselüloz bir çok şeker gruplarını içerir. Biyobozunma, nem absorpsiyonu ve termal bozunma doğal lifteki hemiselüloz yapısıyla bağlantılıdır. Diğer bir önemli bileşen olan lignin ise amorf ve aromatik bir yapıya sahiptir. Termal olarak kararlı olan lignin yapısı en az nem absorpsiyonu özelliğine sahiptir. Lignin yapısının en önemli özelliği ise doğal lif içinde UV bozunmasına karşı sorumlu olmasıdır. Ligninin pamuk lifinin yapısında %0,7-1,6 oranında bulunması bir avantajdır. Doğal lif takviyeli kompozit malzemeler dış ortam şartlarında kullanıldıklarında ultraviyole radyasyonun neden foto bozunmaya uğrarlar. Bu bozunma ilk olarak karakteristik renk değişiminden sorumlu olan lignin yapısında gerçekleşir. Pamuk lifi, lif takviyeli plastik kompozitlerde kullanılabilecek kadar önemli fiziksel özelliklere sahiptir. Fakat literatürde pamuk lifi takviyeli plastik kompozit malzemeler ile ilgili çok fazla çalışma bulunmamaktadır.

Kompozit malzeme üretiminde bir diğer önemli bileşende matris malzemesidir. Matris malzemelesinin en temel görevi lifleri bir arada tutmasıdır. Ayrıca ara yüzeye harici bir yük oluşturur ve ayrıca arayüzeyi çevresel hasarlardan korur. Polimer kompozit malzemelerinde matris malzemesi iki gruba ayrılır: termoplastik ve termoset matris malzemeleri. Termoplastik malzemeler termosetlere göre daha sünek ve daha tokturlar. Polietilen ve polipropilen en önemli termoplastik matris malzemeleri olarak doğal lif katkılı polimer kompozitlerinde kullanılırlar. Düşük yoğunluklu polietilen UV ışığına maruz bırakıldığında mekanik özelliklerini kaybeder ve foto oksidatif bozunmaya maruz kalırlar. Polietilen zinciri üzerinde

oluşan serbest radikaller uzun polimer zincirlerini kırarak daha kısa moleküllere dönüştürürler ve böylece daha gevrek bir polimer malzeme oluşur.

Kompozitlerin dış ortam şartlarına dayanıklılığınına etki eden nedenler termal stabilite, nem dayanımı, mantar dayanımı ve ultraviyole ışına maruz kalmadır. UV ışınına maruz kalma kompozit malzememelerin dayanıklılığı açısında en önemli etkenlerden biridir. Örneğin, UV ışınları kompozit malzemelerde foto bozunmaya neden olurlar ve bunun sonucunda mekanik dayanımda azalma ve kompozit yüzeyinde mikro çatlaklar ve renk değişimi meydana gelir. Foto bozunmayı önlemek için pamuk lifi takviyeli düşün yoğunluklu polietilen kompozitler, birçok düzenleyiciler kullanılarak UV ışığına maruz kalmayı ortadan kaldırmak veya geciktirmek ya da uyarılmış durumdaki moleküllerin enerjisini dağıtarak korunabilir.

Bu çalışmada, ultraviyole absorplayıcı, ışık stabilizatörleri ve antioksidantlar gibi foto dengeleyiciler pamuk lifi takviyeli düşük yoğunluklu polietilen kompozit malzemelerde UV ışığının etkisini azaltmak için kullanılmıştır. Pamuk lifi takviyeli düşük yoğunluklu polietilen kompozit malzemeler tek vidalı ekstruder ile üretilmiştir. CNC freze ile çekme ne darbe numuneleri hazırlamış daha sonra Suntest CPS cihazına konularak UV ışığına maruz bırakılmış ve 120 saat ve 240 saat bekleme sürelerinde örnekler alınmıştır. Katkılı ve katkısız kompozit malzemelerin mekanik özellikleri incelenmiştir ve her biri kendi içlerinde analiz edilmiştir. Foto düzenleyicilerin mekanik özellikler üzerindeki etkisini incelemek için pamuk lifi takviyeli polietilen kompozit malzemelere çekme testi uygulanmıştır. Çekme dayanımı, elastic modulüsü ve kopma uzaması çekme testinden hesaplanmıştır. UV katkısı olmayan kompozit malzemelere kopma uzaması UV ışığına maruz kalma süresi arttıkça azalmıştır. 240 saat UV ışığına maruz kalan kompozit malzemeler içerisinde HALS ile stabilize edilmiş kompozit malzemelerin kopma uzamasında en fazla düşme gözlemlenmiştir. Ayrıca UV absorplayıcılar kompozitlerin mekanik özelliklerini olumlu ölçüde etkilemiştir. UV absorplayıcıların kompozit malzemelerde varlığı kopma uzamasındaki azalmayı düşürmüştür. UV absorplayıcı ile stabilize edilmiş pamuk lifi takviyeli kompozit malzemeler elastic modulüsteki azalmayı önlemiştir.

FTIR spektroskopisi kompozit malzemelerin yüzeyinde meydana gelen kimyasal değişimleri incelemek için kullanılmıştır. Kompozit malzemelerin UV ışığına maruz kalmasından dolayı meydana gelen foto bozunmanın belirlenmesi için karbonil indeks değerleri ölçülmüştür. UV katkısı olmayan kompozit malzemelerde karbonil indeks değerinin en yüksek olduğu gözlemlenmiştir. UV katkılı kompozit malzemelerde ise karbonil indeks değerlerinde azalma gözlemlenmiştir. Karbonil indeks değerlerine bakıldığında, özellikle HALS'ın önemli ölçüde katkısı olduğu belirlenmiştir. Ancak UV absorplayıcıların diğer UV katkılarına göre daha etkili olduğu söylenebilir.

Pamuk takviyeli polietilen kompozit malzemelerin termal özellikleri DSC analizi ile belirlenmiştir. Ayrıca DSC grafiklerinden kompozitlerin kristallinite değerleri hesaplanmıştır. Kristallinite değerleri UV ışığına maruz kalmalarından dolayı kompozit malzemelerdeki polietilen matriksinde meydana gelen zincir kırılmalarına işaret eder. 120 saat UV ışığına maruz kalmış katkısız kompozit malzemelerde polietilen matriksteki zincir kırılmaları zamanla artmaktadır ve bundan dolayı da kristallinite değerlerinde artış gözlemlenmiştir. Ancak 240 saat UV ışığına maruz bırakılan katkısız kompozit malzemelerde ise krisatallinite değerleri polietilen zinciri üzerindeki kısa bağ moleküllerinin kırılmasından dolayı azalır. UV katkılı kompozit

malzemelerde ise 120 ile 240 saat arasında kristallinite değerlerinde çok fazla bir değişim gözlemlenmemiştir. HALS ve AOx katkılı kompozit malzemelerde en iyi sonuçlara ulaşılmıştır.

Ultraviyole ışığına maruz bırakılmış UV katkılı ve katkısız kompozit malzemeler üzerinde renk ölçümü testi uygulanmıştır. Aydınlanma (L*), renksellik koordinatları(a* ve b*) ölçülmüş ve bu değerler kullanılarak renk değişimi(ΔE*) hesaplanmıştır. Bütün kompozit malzemelerde a* ve b* değerleri zamanla azalmaktadır. Δb* değeri kompozit malzemelerin sarılık oranı olarak tanımlanır. 240 saat UV ışığına maruz bırakılan katkısız kompozit malzemelerde Δb* değerinde en fazla azalma gözlemlenmiştir. HALS ile stabilize edilmiş kompozit malzemelerin Δb* üzerinde etkisi olduğu gözlemlenmemiştir. Ancak UV absorber ile stabilize edilmiş kompozit malzemelerde foto beyazlamanın geciktiği gözlemlenmiştir. Ayrdınlanma faktörü olarak tanımlanan ΔL* değeri 240 saat UV ışığına maruz bırakılan bütün kompozit malzemelerde artmıştır. UV katkılı kompozit malzemelerin ΔL* değerleri UV katkısız kompozit malzemelere göre daha düşük olduğu gözlemlenmiştir. AOx ile stabilize edilmiş kompozitlerin aydınlanma değerine etkisinin en büyük olduğu belirlenmiştir. Toplam renk değişimine bakıldığında ise (ΔE) HALS katkılı malzemelerde renk değişimi en az olarak gözlemlenmiştir.

1. INTRODUCTION

The design of materials that are compatible with the environment has influenced from the environmental awareness that has been increasing throughout the world day by day. At present, glass or carbon fibers which are the most common synthetic fibers are widely are used in polymer composites due to their high stiffness and strength properties but besides all these they have several disadvantages such as biodegradibility, initial process cost, recyclability etc[6]. Natural fibers have recently attracted the attention of scientists and technologists because of the potential to act as a biodegradable reinforcing materials alternative for the use of glass or carbon fiber and inorganic fillers[7]. These fibers have several advantages such as high performance in mechanical properties, significant processing advantages, low cost, low density, non-abrasive nature, biodegradability, low energy consumption[7-9]. The most important disadvantage with natural fiber is its hydrophilic character of which leads to a poor adhesion with hydrophobic nature of the polymer matrix[10]. These result poor mechanical and physical properties of fiber composite[11].

Fiber reinforced composites are now being marketed for various applications such as building, automotive and packaging materials. The use of fiber reinforced composites (FRC) have resulted in concern about durability of these products when exposed to outdoor environments [1, 12, 13].

Outdoor durability may include thermal stability, moisture resistance, fungal resistance, and ultraviolet (UV) stability. UV exposure can cause the composites to undergo photo-degradation leading to undersirable effects, including a loss in mechanical properties and surface quality, i.e. surface micro-cracking and color change. The effects of UV radiation on FRC composites can be minimized with the use of photo-stabilizers such as UV absorbers (UVA), hindered amine light stabilizers (HALS-free radical scavengers) and antioxidants. There are many reports available on the literature on the effects of weathering on FRC composites with

respect to changes in appearance, surface chemistry and mechanical properties[1, 12-15]

In this study, cotton fiber (CF)/low density polyethylene(LDPE) composites were manufactured via one-screw extruder. In several composites either HALS, UVA and antioxidant were added. All composites were exposed to accelerated weathering. Mechanical properties and initial changes in surface characteristics and color change of unstabilized and stabilized CF/LDPE composites were determined and compared. The objective of this work to compare the effectiveness of HALS, UVA and AOx in preventing the initial changes in properties of CF/LDPE composite due to accelerated weathering.

2. THEORETICAL PART

2.1 Cotton Fiber

Natural fibers are firstly grouped into two types: wood fibers and non-wood fibers (Figure 2.1). Non-wood fibers are raw materials directly obtainable from a vegetable (cellulosic), animal (proteinic) and mineral source. Of these fibers, jute, ramie, flax and sisal are the most commonly used fibers for polymer composites. The form of wood flour has also been used for preparation of natural fiber composites [16].

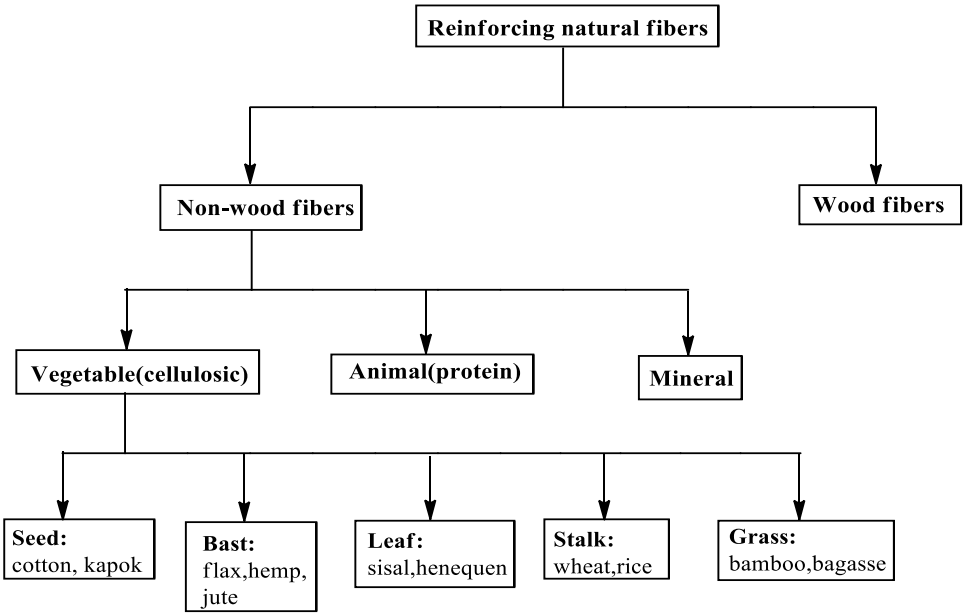


Figure 2.1 : Classification of natural fibers[17]

Natural fibers are mainly made of cellulose, hemicelluloses, lignin, and other substances (Table 2.1). Cellulose (Figure 2.2-a) is the main component of natural fibers and gives the strength, stiffness and structural stability of the fiber. Also, cellulose is semi-crystalline polysaccharide made up of D-glucopyranose units linked together by β-(1-4)-glucosidic bonds. The molecular structure of cellulose determines chemical and physical properties of fibers. These hydrogen groups form

hydrogen bonds inside the macromolecule itself (intramolecular) and between other cellulose macromolecules (intermolecular). Hemicelluloses (Figure 2.2-b) have branched and fully amorphous polymers. They contain different sugar units. Biodegradation, moisture absorption, and thermal degradation of the fiber are mainly related with the structure of hemicellulose. The other important companent of lignocellulosic fibers is lignin (Figure 2.2-c) which is amorphous and has an aromatic structure. Lignin is thermally stable and has the least water absorption but is responsible for the UV degradation. The lignin, hemicellulose and pectin provide the adhesion to hold the cellulose structure of the fiber together [6, 18-20].

Table 2.1 : Structural compositions of natural fibers[18, 21]

Fiber	Cellulose(%)	Lignin(%)	Hemicellulose(%)
Cotton	82.7	-	5.7
Jute	64.4	11.8	12.0
Flax	71	2.2	18.6-20.6
Hemp	57-77	3.7-13	14-22.4
Sisal	65	9.9	12.0
Coir	32-43	40-45	0.15-0.25

Advantages of natural fibers over man-made fiber include low density, low cost, recyclability and biodegradability. These advantages make natural fibers potential replacement for glass fibers in composite materials. Mechanical properties of natural fibers are also important for manufacturing the natural fiber composites[19]. Table 2.2 lists the mechanical properties of some natural and man-made fibers.

Mechanical properties of natural fibers, especially flax, hemp, jute and sisal, are very good and may compete with glass fiber in specific strength and modulus. Besides that cotton fiber is preferred due to the density and chemical structure. Cotton fiber consists essentially of pure cellulose. This structure determines its physical properties. The strength of cotton has been attributed to its highly fibrillar and crystalline structure[22].

Table 2.2 : Mechanical properties of natural fibers [18]

Fiber	Density (g/cm^3)	Elongation (%)	Tensile strength(MPa)	Young's modulus(GPa)
Cotton	1.5-1.6	7.0-8.0	287-597	5.5-12.6
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-3.2	345-1035	27.6
Hemp	-	1.6	690	-
Sisal	1.5	2.0-2.5	511-635	9.4-22.0
Coir	1.2	30.0	593	4.0-6.0
E-glass	2.5	2.5	2000-3500	70.0
Aramide	1.4	3.3-3.7	3000-3150	63.0-67.0
Carbon	1.4	1.4-1.8	4000	230.0-240.0

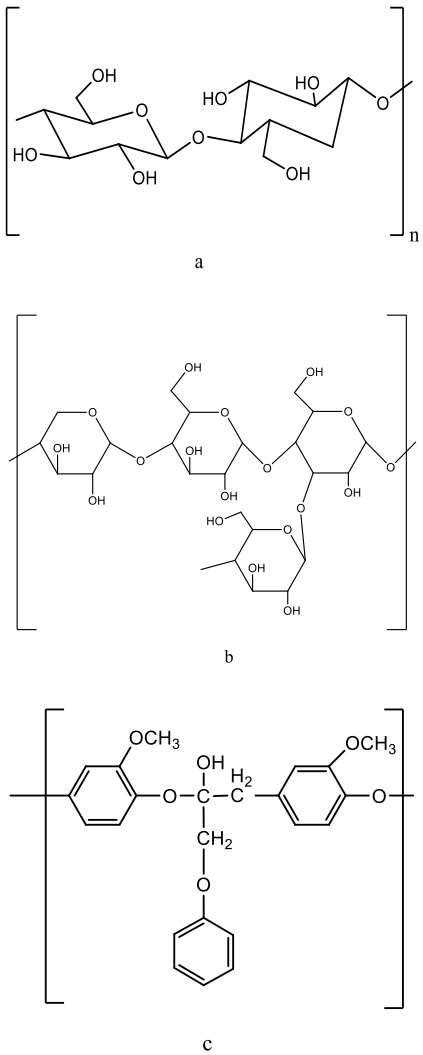


Figure 2.2 : Chemical structure of (a) cellulose (b) hemicellulose and (c) lignin [3]

2.2 Matrix

The matrix is important material to obtain the natural fiber composites. It is used as binder material to hold the fibers in position and transfer the external load to the reinforcement and it protects reinforcement from environmental damage. The reinforcement–matrix interface plays a decisive role in the transferring load from the matrix to the fiber. Matrix materials can be made of metals, polymers or ceramics[6, 20].

Polymer composites are divided into two groups by matrix resin type, thermosets and thermoplastics. Table 2.3 shows the comparision of thermoplastic and thermoset matrices. Thermoplastics are polymers in which cross-links (bonds between molecules) are not present; polymers in which cross-links are present are called thermosets. Thermoset materials once cured cannot be remelted or reformed. During the curing they form three-dimensional molecular networks called cross-links. These cross-linked bonds are as strong as the polymeric backbone chains. Due to these cross-links, thermoset molecules are not flexible and cannot be remelted and reshaped. Thermoplastic materials are ductile and tougher than thermosets and are widely used for non-structural applications without fillers and reinforcements. These low-cost commodity types of thermoplastic resins are nylon, PP, polystyrene (PS), polyethylene (PE), PET and polyvinylchloride (PVC). However, the major processing problems associated with the natural fiber reinforced thermoplastic systems stem from variation in the quality of the natural fiber material, incompatibility between the hydrophilic natural fiber and the hydrophobic matrix and the poor thermal stability of these lignocellulosic fibers at temperatures above 230°C[6, 20, 23].

Table 2.3 : Comparision of thermoplastic and thermoset matrices[6]

	Advantages	Disadvantages
Thermosets	– Low resin viscosity – Good fiber wetting – Excellent thermal stability once polymerized – Chemically resistant	– Brittle – Non-recyclable via standart techniques – Not post-formable
Thermoplastics	– Recyclable – Easy to repair by welding and solvent bonding – Post formable – Tough	– Poor melt flow – Need to be heated above the melting point for processing purposes

2.2.1 Low density polyethylene

Low density polyethylene is one of the type of thermoplastic polyolefin. It is obtained by polymerizing ethylene and it is generally used in film, pipe and cable applications. Figure 2.3 represents to the basic chemical structure of low density polyethylene. Low density polyethylene is susceptible to degradation upon long-term exposure to sunlight, thereby loosing useful tensile properties. Polyethylene is exposed to solar UV radiation readily lose their tensile strength as well as their average molecular weight. The mechanism causing the deterioration is photo-oxidative degradation. The free radical pathway lead to hydroperoxidation and consequent chain scission. The free radicals break polyethylene into shorter molecules resulting in a more brittle polymer[24].

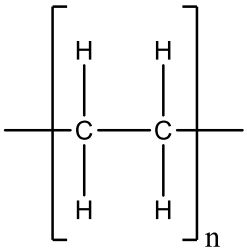


Figure 2.3 : Chemical structure of low density polyethylene[24]

2.3 Natural fiber polyolefin composites

Over the past few decades, natural fiber reinforced polyolefin composites which are reinforcing fibers derived from renewable resources such as wood, sisal, flex etc. have been increasingly used. The main reason for the trend is that natural fibers have many advantages over glass fibers, which are typically used as reinforcement fibers in these industries. While their major advantages are lower cost, lightweight resulting composites, biodegradability and renewable sources, natural fibers have disadvantages such as variations in fiber geometry and physical properties, lower mechanical properties, poor interfacial adhesion and incompatibility with hydrophobic matrix resin systems [4, 23].

2.4 UV degradation of natural fiber composites

Natural fiber polyolefin composites (NFPC) products are susceptible to the UV portion of sunlight. Solar irradiance on these materials causes various deteriorations including color change, fading, surface erosion and loss of gloss, which reduce product lifetime. Under UV exposure, surface chemistry of the composite changes due to photodegradation, which leads to discoloration of the product, making it aesthetically unappealing. Stark and Mantuana also suggested that prolonged UV exposure might also lead to the development of fracture in the product and make the product more vulnerable to other weathering elements in the surroundings such as water and wind, which ultimately result in mechanical failure of the product. So, UV radiation is one of the major practical problems that NFPC products encounter in outdoor applications[1].

Stark studied the changes in wood flour/high-density polyethylene (HDPE) composites after accelerated weathering with and without water spray. Injection molded and extruded HDPE composites filled with 50-wt% wood flour were used. It was found that exposure to UV light resulted in an increase in flexural modulus of elasticity (MOE) for the injection molded composite because of less wood at the surface, whereas a decrease in flexural MOE (12%) for extruded composite with more wood at the surface. From this study, it has been suggested that the processing method of wood-polymer composites (WPCs) affects the degradation by UV exposure[25].

Selden et al. studied the effect of accelerated UV aging on properties of wood fiber/PP composites with different fiber content. The composite samples containing 3% UV stabilizer were subjected to accelerated UV aging in a QUV weatherometer for up to 8 weeks. With regard to mechanical properties, their results showed that the wood fiber/PP composites displayed good UV resistance; however, physical and chemical analyses (differential scanning calorimetry, DSC; Fourier transform infrared, FTIR; and scanning electron microscopy, SEM) of the surface layers of the composite showed the occurrence of PP matrix degradation. By increasing the fiber, content from 25 to 50-wt% the rate of degradation of the composite increased by approximately a factor of two as the number of chromophores (light-absorbing groups) increased with increased fiber content. The melting temperature of the composite also decreased by 33% in the case of 50% wood fiber content and was explained as being due to molecular chain scission and the formation of carbonyls and hydroperoxides[26].

Discoloration and surface roughness are the characteristic degradation features of UV exposure of NFPC. In one of the studies by Sharma et al. surfaces of coir/PP laminates showed a slight change in surface roughness after 10 h of UV exposure; however, with increased exposure time of 20h, the surfaces started to turn white and after 200 h of exposure, the surfaces became very rough and chalky with clearly visible fibers[27].

In wood-fiber/PP composites, Selden et al. observed that the color of the composite changed from brown to chalky white at the exposed area for 50-wt% wood-fiber content after 8 weeks of accelerated UV aging. This was explained as being due to PP matrix degradation resulting in chemi-crystallization and extensive surface cracking[26].

2.4.1 Mechanism of degradation

The components of natural fiber polyolefin composites (NFPC), natural fiber and plastic, absorb UV radiation of different wavelengths leading to free radical photo-oxidation and undergo thermo-oxidation as a result of increased temperature. Polymer degradation through photo-oxidation has been studied in different materials by various researchers around the world. Discoloration, i.e. photo yellowing and photo bleaching of NFPC products, has been proved to be caused by light at different

wavelengths. According to Hon, lignocellulosic materials such as wood and paper readily undergo light-induced photo-yellowing[28]. Lignin, which is a major constituent of natural fiber, contains chromophores which readily absorb UV radiation[29]. According to Rowell, lignin, which is responsible for holding the cellulose fibers together, degrades owing to exposure to UV radiation, making the surface richer in cellulose content. After lignin degradation, the poorly bonded fibers erode easily from the surface, exposing new lignin to further degradation. With time, this degradation process makes the composite surface rough and accounts for a significant loss in surface fibers, and hence composite properties[30].

In another study made by Winandy et al[31] for recycling consideration of wood-plastic composites (WPC), it has been stated that the surface of the WPC oxidizes upon UV exposure. Owing to the presence of oxygenated functional groups, polyolefins are responsible for further photo-oxidation that results in a decrease in tensile strength and elongation[32]. It has been also shown[1] that the properties of WPC degrade by the addition of wood to plastic due to the formation of further oxidation sites.

Sharma et al. studied the effect of UV and moisture on the surface of coir/PP laminates and suggested that the discoloration and surface roughness in the laminates was due to complex processes of photochemical degradation of polymers, hydrolysis, and oxidation. Free radical formation occurs at the surface of the laminates as the UV light absorption provides the energy to the polymer for breaking molecular bonds, such as $C{=}C$, $C{-}H$, $C{=}O$. In the case of coir/PP laminates, the PP forms free radicals owing to the presence of a large number of tertiary carbon sites. These free radicals form peroxy radicals by reacting with oxygen, which attack the polymer molecules in the laminates and change the color of the laminate from white to yellow. Coir fibers also undergo UV degradation through free radical reactions with the decomposition of polymer in the cell wall. The surface area increases as the composite swells, which allows more material to be UV exposed and more moisture to be absorbed, therefore changing the color from brown through bleaching to white. The same authors also studied the effect of UV and moisture on glass/PP laminates and found that as glass fiber is inert to UV radiation, the color change of laminate is from opaque white to yellow because of PP reactions only[27].

2.4.1.1 Photodegradation mechanism of polyethylene

Polyolefins are susceptible to photo-oxidation under the exposure of UV radiation due to the presence of chromophores. The reaction mechanism of the oxidation process in polyolefins follows Figure 2.4. The free radicals formed in the initiation stage attack the polymer in the propagation stage and form new free radicals. In the termination stage, two free radicals combine together and seize the reaction[29].

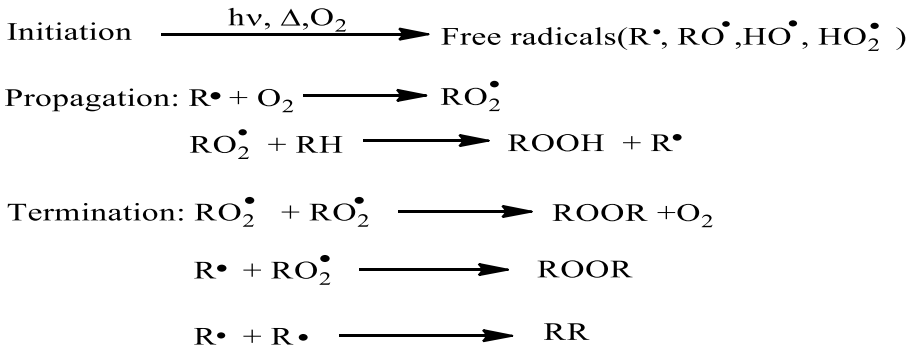


Figure 2.4 : Sequence of oxidation reactions in polymers[29]

During the initial stage of UV exposure, vinylidene and hydroperoxide concentrations act as initiators of photo-oxidative degradation, where as at the later stage, carbonyl groups act as auto-accelerating photoactivators. It has been reported that the degradation of carbonyl groups occurs according to Norrish type I (Figure 2.5) or II (Figure 2.6) reactions[33].

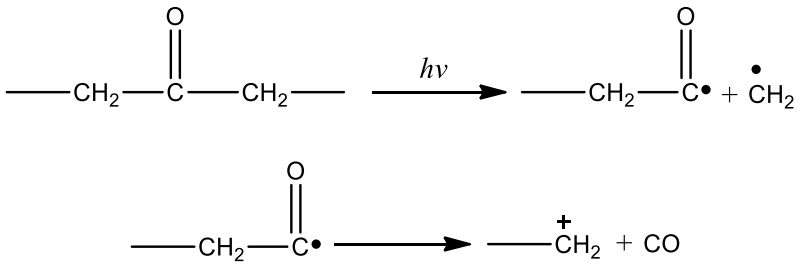


Figure 2.5 : Norrish type I reaction[29]

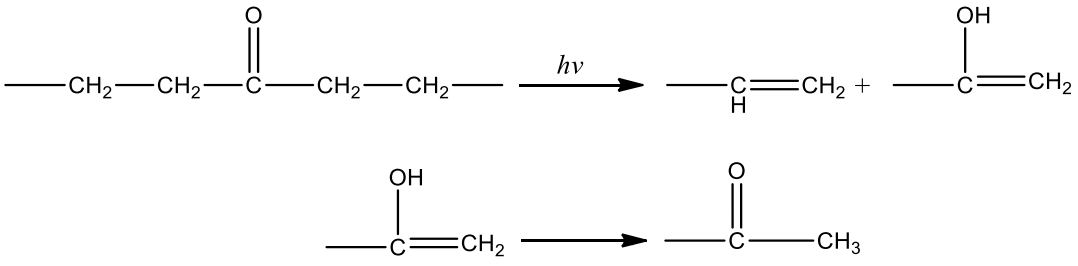


Figure 2.6 : Norrish type II reaction[29]

In the Norrish type I reaction, the free radicals which are carbon monoxide and macro radicals form according to Scheme 1. In the Norrish type II reaction, carbonyl and terminal vinyl groups are produced and lead to chain scission. Furthermore, the carbonyl groups formed may undergo further degradation. Chain scission and crosslinking are found to be competing reaction mechanisms during UV degradation of polyethylene [12, 34, 35]. However, chain scission is proved to be more dominant in natural weathering[36]. The researchers[35, 37] argued that the formation of carbonyl groups and vinyl groups is the indicator of chain scission. Another indicator of chain scission is the increase in polyethylene crystallinity after weathering [35]. The chain scission produces shorter chains with high mobility that crystallize more readily, resulting in increased crystallization and associated embrittlement of the polymer. The chain scission occurs in the amorphous phase of the polymer, but imperfect crystalline regions degrade because of crosslinking [29].

2.4.1.2 Photodegradation mechanism of natural fibers

Lignin, one of the major constituents of fiber, breaks down into water-soluble products due to UV exposure and generates light absorbing species, chromophoric functional groups such as carbonyls, carboxylic acids, quinines, and hydroperoxide radicals[29]. Various reaction pathways have been suggested [29, 38] for chromophoric structure formation from lignin decay, which cause photoyellowing of lignin, out of which the phenacyl, phenoxy and the singlet oxygen pathways initiated by the excitation of the carbonyl group.

In addition to these pathways, free radical ketyl reaction and redox cycle [29, 38] are also responsible for chromophore formation. In phenoxyl quinone redox cycle (Fig. 2.7), hydroquinone structures undergo oxidation to form paraquinones, which are chromophoric structures, resulting photoyellowing of lignin. In the reverse cycle paraquinones reduced to hydroquinones, causing photobleaching of lignin.

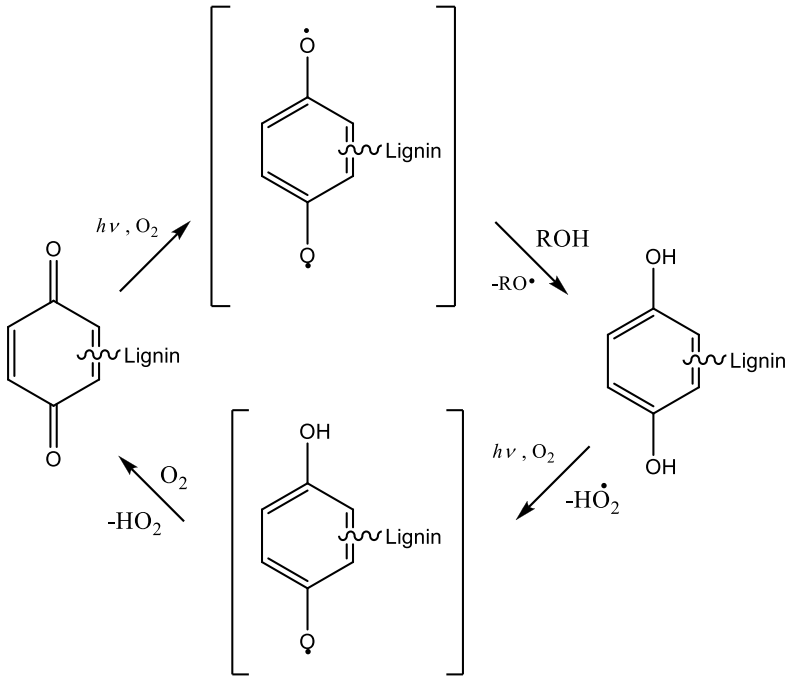


Figure 2.7 : Redox cycle involved in photo-yellowing of lignin[39]

2.5 Manufacturing of natural fiber composites

Processing techniques of natural fibre composites are similar to those utilized in processing synthetic fibres. Depending on the length, orientation and type of the fibre, randomly oriented (short), unidirectional (raw and carded) and woven fabrics are used as reinforcements in thermoset and thermoplastic matrices.

For thermoplastic matrices, application of the direct impregnation ("wet" processing) is limited by relatively high viscosity of thermoplastic polymer solutions or melts. For this reason, "prepreg" processes with preliminary fabricated tapes in which fibers are already combined with thermoplastic matrix are used to manufacture composite parts. There also exist other processes that involve application of heating and pressure to hybrid materials including reinforcing fibers and a thermoplastic polymer in the form of powder, films or fibers. A promising process (called fibrous technology) utilizes tows, tapes or fabrics with two types of fibers - reinforcing and thermoplastic. Under heating and pressure thermoplastic fibers melt and form the matrix of the composite material[40].

While injection molding is the largest process in the plastics industry in terms of number of plastic fabricating machines operating, extrusion is by far the largest in terms of volume of material processed. In the extrusion process, a granulate is

converted to a high viscosity paste by heat and pressure. The basic components of the extruder are shown in Figure 2.8. In this technique, plastic pellets are fed into the feed throat from the hopper. As the unmelted substance exits the feed throat, it comes into contact with a rotating screw. The extruder screw is contained within a heated barrel, which is maintained at a higher temperature than the screw. Since the plastic tends to adhere to hotter surfaces, the unmelted materials will stick to the barrel and slide onto the screw. As the plastic moves forward, it is heated by the barrel in addition to the frictional heat generated by the compounding and compression actions of the screw. By the time the plastic melt leaves the screw and the barrel, it has been melted, compressed and mixed into a homogeneous melt. Short fibre composites can be fabricated into useful parts by extrusion and moulding[41, 42].

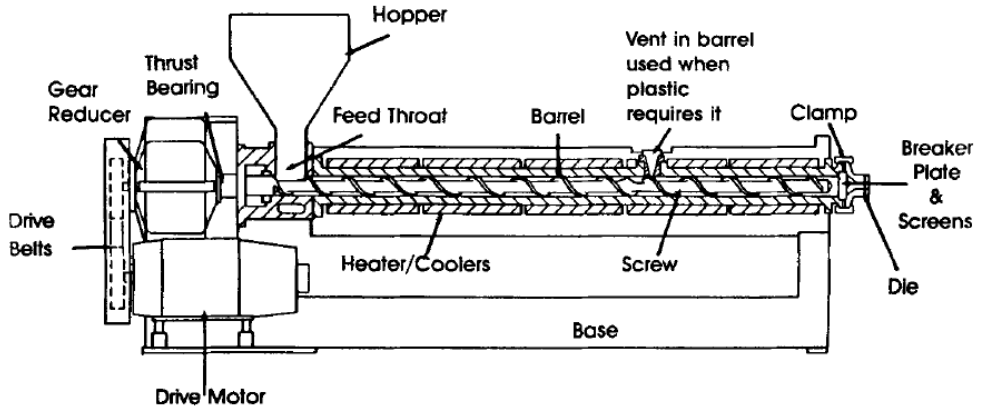


Figure 2.8 : A typical single screw extruder with continuous melt flow[41]

2.6 Weathering of composites

Weatherability tests are intented to evaluate polymer performance in an outdoor environment. Degradation during outdoor exposure is influenced to varying degrees by all of the phenomena associated with natural weather conditions. Heat, radiation(UV and IR), rain and atmospheric contaminants all contribute to degradation of polymers when exposed out-of-doors The effectiveness of these factors depends upon the geographical location of the testing place and its elevation above sea level. Thus the testing of outdoor stability presents many complex problems. Any single phenomenon, e.g. uv radiation, can be maximized in the selection of an exposure site, but other contributing factors may not be intensified to the same degree[43, 44].

The plastics industries require rapid answers on product ageing in environmental and/or aggressive conditions. They continuously demand the develop ment of accelerated ageing tests which allow prediction of the behaviour of materials in working conditions. It is difficult to find correlation between accelerated test methods and outdoor ageing in service conditions. The main reason for this is the lack of correlation between physical and mechanical properties of different polymers and formulations of plastics materials, measured by different methods and in different experimental conditions. There is still no mathematical model which can describe accelerated and outdoor ageing taking into account all the parameters which influence these ageing processes[45].

Accelerated weathering devices have different types of light sources and configuration and include, for example, combinations of fluorescent lamps, xenon arc or carbon arc, and operate in the presence or absence of a combination of other factors, e.g. humidity, temperature, dark and light cycles[46].

2.7 UV Additives

Polymers encounter the oxidation reaction which is present in every stage of the life cycle of polymer from synthesis/manufacture to processing, such as extrusion, molding etc. Even this oxidation reaction presents in the final usage by the customers and is not only seen as discoloration but also the induced loss of gloss or transparency, chalking and surface cracks. Oxidation reactions are the major cause of polymer degradation and is responsible for the ultimate mechanical failure of polymer artifacts. There are some oxidations reactions of polymers like chain scission, crosslinking, or formation of oxygen containing functional groups and their degradation products. Chain scission results in the loss of molecular mass, increase in melt flow, and decrease in toughness. Crosslinking increases molecular mass, decreases melt flow and increases toughness in the early stage[47-49].

Photooxidative degradation of polymers is initiated by the action of photons on the polymer. The following autoxidation proceeds, however, analogous to the already described autoxidation chain of reactions. The possibilities available for the inhibition of photon induced degradation are shown in Figure 2.9 [50].

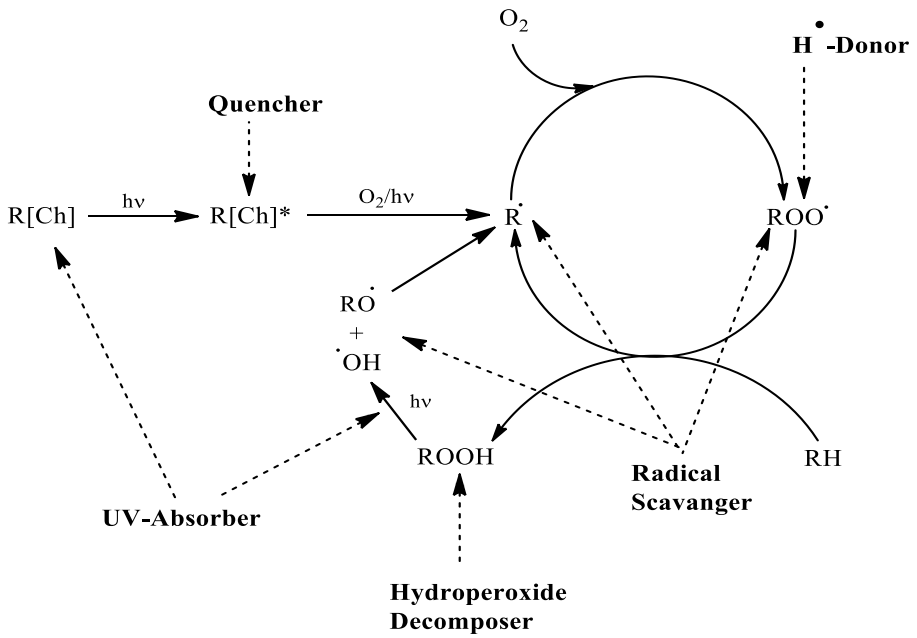


Figure 2.9 : Photo-oxidative degradation process[50]

By the use of suitable UV absorbers incorporated into the polymer, the penetrating light is absorbed and extremely rapidly deactivated by, e.g., transforming it to thermal energy by radiationless processes. These processes compete with the light-induced reactions of the polymer such as the photolysis of hydroperoxides, Norrish type I and type II reactions. The use of so-called "quenchers" deactivates the excited chromophores such as the carbonyl groups in polymers formed by thermo oxidation. The latter, as shown, are efficient sensitizers for the photolysis of hydroperoxides. Finally, radical scavengers and hydroperoxide decomposers could be used in the same way as for the inhibition of thermally initiated autoxidation for the prevention of the chain reaction[50].

2.7.1 Antioxidants

Antioxidants are used in plastics to inhibit their oxidative degradation. The thermal oxidation can be inhibited by antioxidants. The thermal degradation is also prevented during processing and under atmospheric aging by the addition of antioxidants. Antioxidants can retard the free radical reactions occuring during auto-oxidation reactions. Since the chain reaction of auto-oxidation proceeds in a similar way under thermooxidative and photooxidative conditions, the use of phenolic antioxidants should also contribute to stabilization under photooxidative conditions. The

photochemically induced formation of phenoxly radicals competes with the stabilization of the peroxy radicals, $ROO^{\cdot}$ by transfer of hydrogen from the phenolic group resulting in the hydroperoxide, ROOH. Strengthening of the OH-bond by suitable substituents leads to improvement of the photo stability hindered phenols. Antioxidant may also affect the crosslinking reactions [48-50].

Without antioxidant, particularly with polyolefin, there is not only discoloration but also an induced loss of gloss or transparency resulting in chalking and surface cracks. However, antioxidant degradation may be a potential source of color formation in plastics. Sometimes other additives can also cause discoloration. Hence major discoloration with oxidation is prevented by the addition of antioxidants as additives in plastics[51].

Antioxidants cover different classes of compound which can interfere with the oxidative cycles to inhibit or retard the oxidative degradation of polymers. Figure 2.10 shows an outline of the two major antioxidant mechanisms. There are two types of antioxidants: primary and secondary antioxidants.

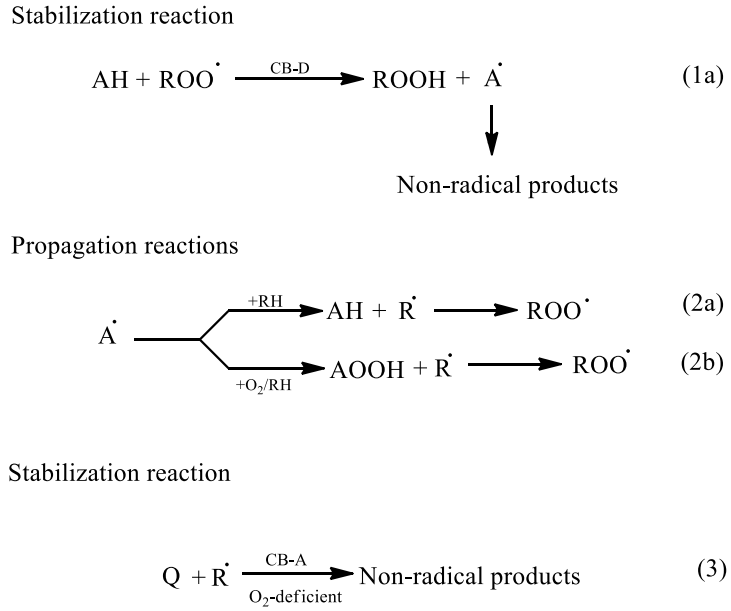


Figure 2.10 : Reactions of two major primary antioxidant mechanisms[49]

- Primary antioxidants are radical scavengers or hydrogen donors or chain reaction inhibitors which include hindered phenols and secondary amines.

- Secondary antioxidants (preventive antioxidants) are peroxide decomposers and are composed of organic phosphates and thio-esters[49].

Primary antioxidants sometimes referred chain breaking antioxidants which interrupt the primary oxidation cycle by removing the propagating radicals, ROO· and R·. Two main classes of chain breaking antioxidant are: chain breaking donor (CB-D) and chain breaking acceptor (CB-A). Figure 2.10 shows the primary antioxidants (CB-D and CB-A) mechanisms. Chain breaking donor antioxidants (CB-D) are electron or hydrogen atom donors which are capable of reducing ROO· to ROOH, see reaction 1a. To perform their function, CB-D antioxidants must however be able to compete effectively with the chain propagating step and the antioxidant radical (A·) produced from reaction 1a must lead to stable molecular products, i.e. .(A·) does not continue the kinetic chain either by hydrogen abstraction (reaction 2a) or by reaction with oxygen (reaction 2b). Hindered phenols and aromatic amines are important examples of commercial CB-D antioxidants. Chain breaking acceptor antioxidants (CB-A) act by oxidizing alkyl radicals in a stoichiometric reaction (R" are removed from the autoxidizing system in competition with the chain propagating reaction, and hence are only effective under oxygen deficient conditions); see reaction 3. Quinones and stable free radicals which can act as alkyl radical trapping agents are good examples of CB-A antioxidants [49].

Addition of primary and secondary antioxidants provides the polymer with the advantages of synergistic effects. A single antioxidant cannot provide all the different properties required in a polymer application. Commercially available antioxidants are based on combinations of two or more[48].

Hindered phenols are generally called chain breaking donor antioxidants. The chain-breaking donor (CB-D) mechanism, on the other hand, operates when substantial oxygen concentrations are present," and consequently high concentrations of alkylperoxyl radicals. Single electron donors (reducing agents) or compounds which, after donation of a labile hydrogen (to RO_2), give rise to a stable (non-propagating) radical, are therefore used as CB-D antioxidants[48].

Hindered phenols are the most widely used stabilizers for polymers. The key reaction in the stabilization of polyolefins by phenolic antioxidants is the formation of

hydroperoxides by transfer of a hydrogen from the phenolic moiety to the peroxy-radical resulting in the phenoxyl-radical(Figure 2.11) [50].

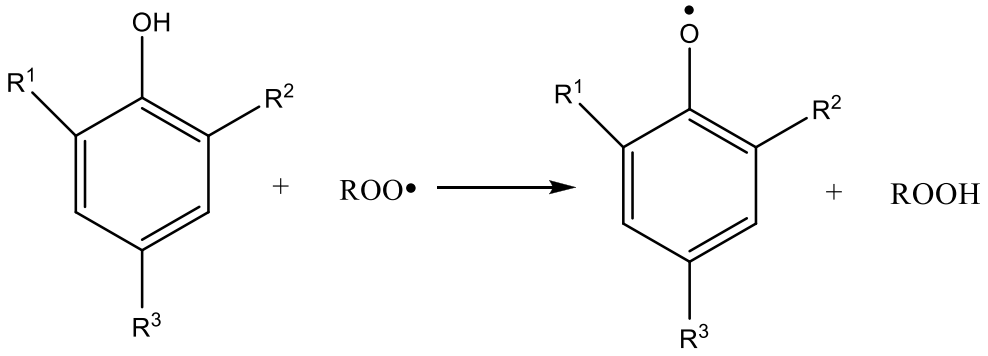
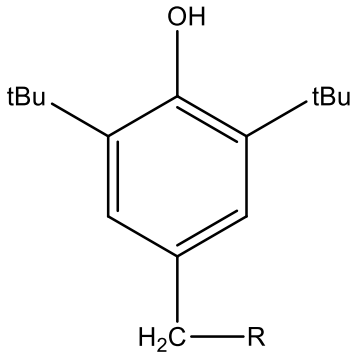


Figure 2.11 : Transformation of peroxy radicals into hydroperoxides by hindered phenols[50]

The efficiency of an antioxidant increase with increasing of the substituents. Sterically hindered phenols are capable of preventing the abstraction of a hydrogen from the polymer backbone. The reactivity of the formed phenoxyl radical is significantly influenced by the substituents in 2- and 6- position. Bulky substituents prevent the reaction of the phenoxyl radical with the polymer. The rate of hydrogen abstraction from phenol increases with decreasing steric hindrance in 2- and 6-position. Sterically hindered phenols can be classified as follows: Fully sterically hindered phenols and partially hindered phenols[50].

The basic requirement for an effective photoantioxidant is that it should not be lost by physical means (because of its high solubility, diffusion, volatility and/ or extractability) from the polymer and that the parent antioxidant and its transformation products (formed during melt processing and thermo- and photo-oxidation during in-service) are photostable under continuous exposure to UV light; they must not be lost or transformed into sensitizing products. Other factors, which can affect the ultimate photostability of polymers, are : sample thickness; polymer crystallinity; and the presence of other additives, e.g., pigments and fillers. For example, chain breaking donor (CB-D) antioxidants such as the hindered phenols are relatively ineffective under photo-oxidative conditions as they are generally unstable to UV light and some of their oxidative transformation products. However, both the hindered phenols and these sulphide antioxidants can synergize with UV stabilizers and become much more effective photoantioxidants.

The basic structure is the hindered phenols is shown in Figure 2.12. When R group is $-(CH_2CO_2CH_4)_4C$ it is called Irganox 1010 on the commercial scale which is generally used in commercial area [50, 51].



(AH)

1 BHT

R= -CH
R= $-CH_2CO_2C_{18}H_{17}$
R= $-(CH_2CO_2CH_4)_4C$

2 Topanol O
3 Irganox 1076
4 Irganox 1010

Figure 2.12 : The basic structure of hindered phenols[51]

Chain-breaking donor antioxidants are therefore generally less effective than CB-A antioxidants as melt stabilizers. However, they are still used for melt stabilization because they are cheap and relatively non-discolouring additives. Thus, under normal processing conditions, both alkyl and alkylperoxyl radicals can coexist (albeit at different concentration levels)[51].

2.7.2 UV Absorbers

Ultraviolet absorbers are the most widely used category of photostabilizers. They are substances that absorb a given portion of the natural light spectrum, the energy of which is high enough to induce polymer degradation by initiating primary free radicals or by decomposing hydroperoxides. Also, UV absorbers are colourless compounds characterized by high extinction coefficients in the spectral range of 300-400 nm. There are two key requirements for this type of UV absorber:

1) The additive must absorb radiation that would degrade the polymer, and

2) It must dissipate the absorbed energy by a mechanism which does not promote polymer degradation. Miscibility, retention, resistance to degradation and cost are also important in the selection of a UV absorber [44, 50, 52].

The most common UV absorbers are low-molecular-weight derivatives of o-hydroxybenzophenone and o-hydroxybenzotriazole. Hydroxybenzophenones are generally believed to function by converting UV energy into vibrational energy within a hydrogen bond. The key to this process lies in the ability of these compounds to form a six-membered ring containing a hydrogen bond. The o-hydroxyphenylbenzotriazoles probably also dissipate absorbed energy by this mechanism[44].

Hydroxyphenyl benzotriazoles (Figure 2.13) have the following general structure where X is H or Cl chlorine shifts the absorption to longer wavelengths), R is H or alkyl, R' is alkyl (R and R' increase the affinity to polymers).

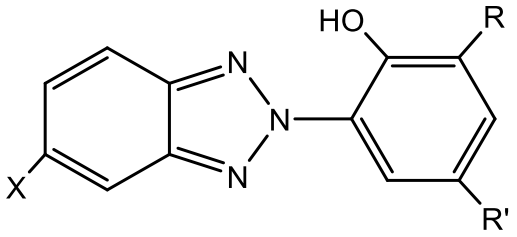


Figure 2.13 : General structure of hydroxyphenylbenzotriazole [52]

Hydroxybenzotriazole derivatives generally absorb in the 280-300 nm range. The tendency to form chelated rings by the creation of hydrogen bonds between hydroxide and carbonyl groups or groups containing nitrogen is a characteristic property of all UV absorbers. The exact mechanism of light absorption by hydroxybenzotriazoles is not known; however, the formation of intramolecular hydrogen bond and of zwitter ions having a quinoid structure may be responsible for the transformation of light radiation energy into chemical modifications [52].

Hydroxybenzotriazole mechanism is shown in Figure 2.14. By absorption of light, UV absorbers are transformed into an excited state, which, by rapid intramolecular processes, is deactivated and returned to its original state. Consequently, the energy imposed on the polymer matrix cannot initiate the damaging, photo oxidative reactions. The efficiency of a UV screening agent in a non-light-absorbing substrate, e.g. PE-LD, PP, depends on the concentration of the UV absorber used and the thickness of the polymer [44, 50, 52].

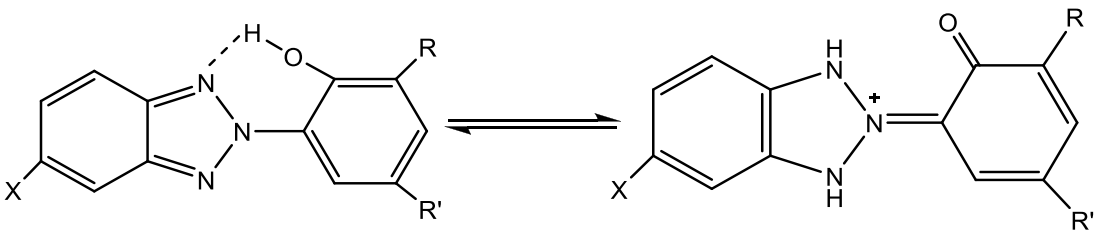


Figure 2.14 : Hydroxybenzotriazole mechanism[44]

Numerous studies are published in the literature regarding the function of UV-absorbers. UV absorbers may develop objectional color in some polymers during processing for exposure to sunlight. When color stability is essential, the more stable though more expensive, o-hydroxyphenylbenzotriazoles might be preferred[44].Ping et al.[5] reported that the addition of benzotriazole type of UVA significantly decreases lightness and yellowness with exposure time compared to the benzophenone UVA. It is stated that the benzotriazole UVA has a higher UV absorbance between 320 and 400nm while is defined as UV-A spectral regions. Benzophenone UVA has a lower UV absorbance 290 and 400nm which is defined as UV-B spectral region. Because much of the electromagnetic radiation in the UV-B spectral regions is absorbed by the ozone layer before reaching the ground and mainly UV-A radiation reaches the earth's atmosphere. Therefore, it is expected that benzotriazole UV absorber is better resentence to discoloration than benzophenone UV absorber.

Hua Du et al studied the effects of UV absorbers on the ultraviolet degradation of rice-hull/high density polyethylene composites [53]. According to SEM analysis, surface cracks were apparent for all of the rice-hull/HDPE composites after 2000h of UV exposure. However, cracks in the composites containing UV absorbers appeared to be less severe than in those without UV absorbers. The UV absorbers protected the rice-hull/HDPE composites from UV degradation to a certain extent, with benzotriazole being more effective than benzophenone.

In another study, Stark et al. examined the surface chemistry of wood-flour/HDPE composites after accelerated weathering[35]. FTIR was used to determine functional groups present on the surface of the composites before, after 1000h, and after 2000h of weathering. It is stated that the growth in surface oxidation from 1000 and 2000h of weathering was significant only for composites without UVA.

2.7.3 Hindered amine light stabilizers (HALS)

Hindered amines are the category of photostabilizers to become available for the protection of polymers against UV degradation. Although the mechanism by which hindered amines protect against photodegradation is complex and has not as yet been completely established, radical trapping is generally agreed to be a major component of the process. Originally developed as photostabilizers for polyolefins, hindered amine light stabilizers (HALS) are now used to protect many other classes of polymers. There is considerable interest in these compounds because of their high level of efficiency at relatively low concentrations [44]. The sterically hindered amines are extremely efficient stabilizers against the light-induced degradation of most polymers (the original name: Hindered Amine Light Stabilizers). Unlike UVabsorbers, and to a certain extent quenchers, sterically hindered amines do not absorb in the range 300-400 nm. Their effectiveness against light-induced degradation of polymers, particularly of polyolefins, led to a revolution in stabilization [50]. HALS stabilizers, depending on their chemical structure, can exist as liquids or solid powders. They are colorless compounds, and except in the case of specific interactions with some other additives do not affect the color of the final product article. Most of the HALS stabilizers do not absorb in the UV wavelength region of terrestrial solar radiation[43].

The most common group of hindered amine light stabilizers originates from 2,2,6,6-tetramethylpiperidine (Figure 2.15). HALS include a number of other structurally different hindered amines. Further substitution of the piperidine ring is employed to improve compatibility of the additive with the polymer and to enhance long-term retention of the additive during ageing of the polymer[43].

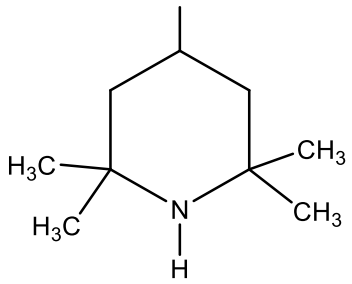


Figure 2.15 : The most common group of hindered amine light stabilizer[43]

Several mechanisms have been suggested to account for photostabilization by hindered amines[44]. It is written that a mechanism involving reaction between HALS compounds and hydroperoxides, formed in the polymer, to yield stable nitroxyl radicals which are believed to be responsible for stabilization. These nitroxyl radicals, which apparently form in the early stages of reaction, are very effective scavengers of alkyl or macroalkyl radicals but not peroxy radicals. Substituted hydroxylamines (X) are formed in this reaction (Figure 2.16).

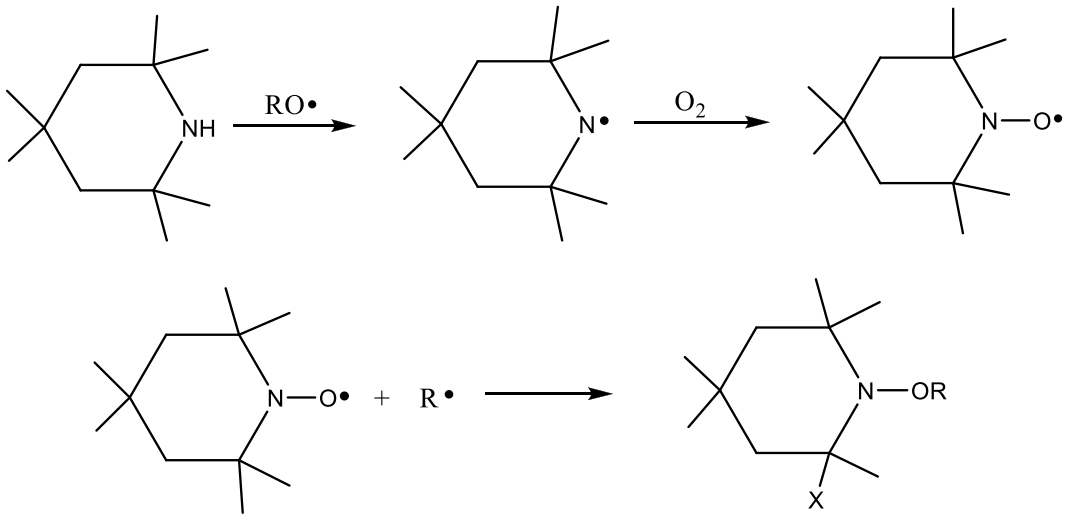


Figure 2.16 : The reaction of substituted hydroxylamines[44]

It has also been suggested that singlet oxygen can convert hindered amines into nitroxyl radicals. It is evident that HALS compounds can inhibit polymer degradation in several different ways. The ability of hindered amines to react with hydroperoxides and of nitroxyl radicals to trap alkyl radicals suggests a role in protecting against thermal oxidation. The substituted hydroxylamines (X) can react with peroxy radicals, to regenerate nitroxyl radicals (IX) (Figure 2.17).

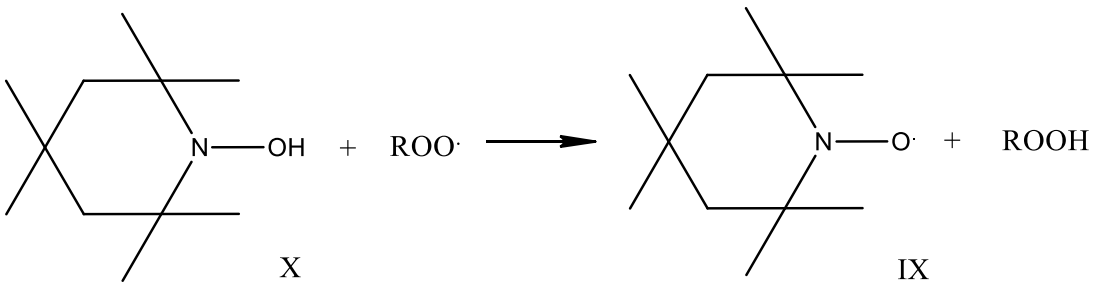


Figure 2.17 : The reaction of substituted hydroxlamines with peroxy radicals[44]

HALS compounds may also protect by deactivating excited states in polymer molecules. For nitroxyl radicals to function effectively as radical traps, they must

compete with oxygen in scavenging alkyl radicals. It was also found that the reaction of polymer radicals with nitroxyl radicals is about twenty times slower than with oxygen. However, regeneration of nitroxyl radicals as shown above could alter this ratio. Substituted hydroxylamines, on the other hand, react with peroxy radicals at a rate about a hundred times faster than these radicals react with hydrogen at branch sites in polypropylene. These authors have concluded that although radical scavenging by nitroxyl radicals and by substituted hydroxylamines can account for the effectiveness of some HALS compounds, other reactions must also contribute to the photostabilization of polypropylene. They suggest that association of the stabilizer or its reaction products with oxidation sites in the polymer could be an important reaction in the stabilization of polypropylene[44].

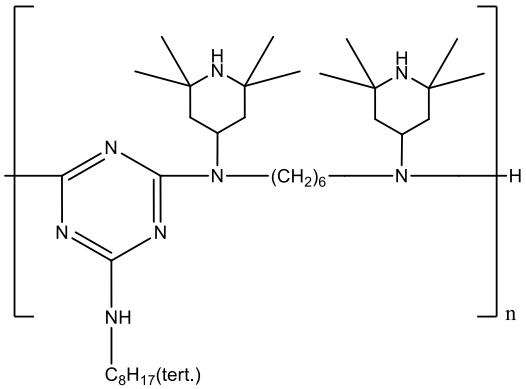
Although polyethylene is less sensitive to UV degradation than polypropylene, it requires good light stabilization for outdoor applications. LDPE and LLDPE are usually stabilized with oligomeric HALS alone; in some cases combinations with benzophenone UV-absorbers are recommended. HDPE can be well stabilized by low molecular weight HALS as well as by oligomeric HALS; but in general, oligomeric stabilizers are often preferred[46].

Xue et al. studied that the effect of photostabilizers on surface color and mechanical property of wood-flour/HDPE cmposites after weathering[5]. It is stated the difference in molecular weight of HALS has a significant effect on color stability and mechanical property of the composites. HALS with high mechanical weigth is not easily diffusing to the surface of the composites and not easily evaporates with longer exposure time. In this way, high molecular weight HALS exhibit greater ability to stabilize the color and decrease the loss of flexural property than the low molecular weight HALS.

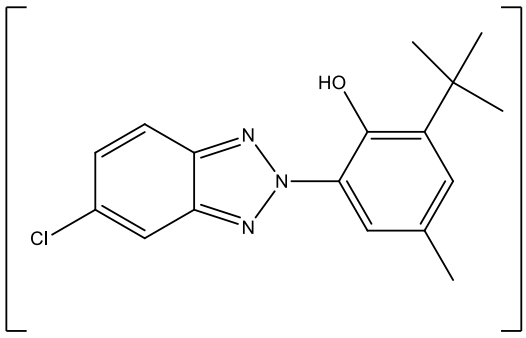
3. EXPERIMENTAL PART

3.1 Materials

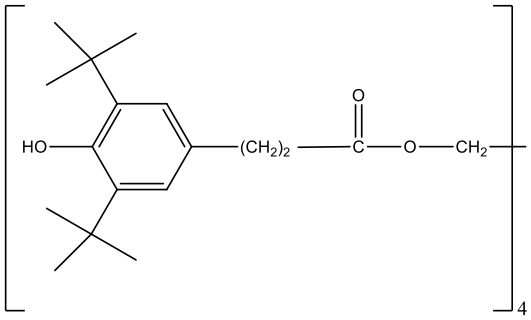
Untreated composites and composites with different chemical treatments were manufactured with 25 wt% waste cotton fabrics. Chopped waste fabrics are rib knitted, 30 Ne yarn and 100% cotton supplied by Linens Marketing Inc., Turkey. Matrix material of the composite is low density polyethylene (LDPE) supplied from Petkim Inc., Turkey. Chimmasorb 944, Tinuvin 326 and Irganox 1010 (Figure 3.1) are used as a HALS, UVA and antioxidant, respectively. Also, Figure 3.2 shows the concentration of materials to obtain cotton fiber reinforced LDPE composites.



Chimmasorb 944



Tinuvin 326



Irganox1010

Figure 3.1 : Chemical structures of UV additives[1, 33, 51, 54]

Sample names	Cotton fiber(%)	LDPE(%)	HALS(%)	UVA(%)	AOx(%)
CF/LDPE	25	75	-	-	-
CF/LDPE/HALS(0,5%)	25	74.5	0.5	-	-
CF/LDPE/HALS(1%)	25	74	1	-	-
CF/LDPE/UVA(0,2%)	25	74.8	-	0.2	-
CF/LDPE/UVA(0,4%)	25	74.6	-	0.4	-
CF/LDPE/AOx(0,5%)	25	74.5	-	-	0.5
CF/LDPE/AOx(1%)	25	74	-	-	1

Figure 3.2 : Ratios of components in the composites

3.2 Processing of composites

25 wt% cotton fabric reinforced composites were manufactured by using a custom made single screw extruder. At the end of the extruder, a special die was used to manufacture composites in the plate form with the thickness of 6 mm. The remaining plates were granulated for the next processing step (reprocessing). Reprocessing process was performed for three times to turn the waste cotton fabrics into the cotton fibers and to provide better fiber homogeneity in matrix [55]. After the

manufacturing process, composite plates were pressed to maintain constant thickness and flatness. Samples for tensile and impact testing were cut out of from the calibrated plates by using a desktop CNC milling machine (Figure 3.3).

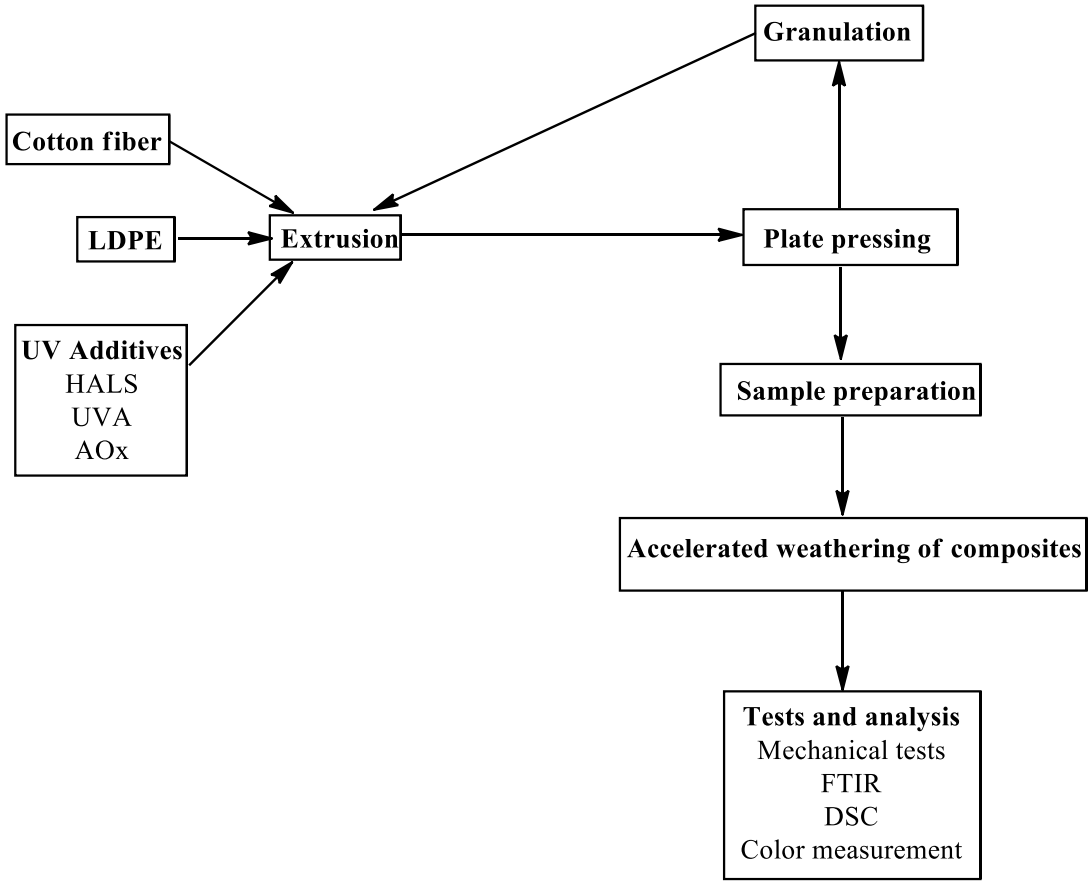


Figure 3.3 : Basic composite manufacturing and flow chart of the study

3.3 Weathering of composites

The composites were performed in the Suntest CPS equipment (Heraeus Industrietechnik GmbH, Germany). Composites were exposed to wavelengths of light higher than 340nm, using a Xenon light source with energy density 300W/m^2 at 30^{o}C for 120h and 240 h of exposure.

3.4 Tensile testing

Tensile testing was performed according to ASTM D638–08: Standard Test Method for Tensile Properties of Plastics. Static tensile tests were conducted in the laboratory where the temperature was at 23 ˚C and had 50 % relative humidity. The

specimens were tested by using a Shimadzu AG-IS tensile testing machine fitted 50 kN load cell operated at a cross-head speed of 50 mm/min. Optical extensometers followed by two digital cameras were used to measure strains.

3.5 Impact testing

Impact testing was carried out according to EN ISO 179: 1997 with the specimens had the "type A" single notch. Test specimens were tested by using Devotrans Charpy impact testing device with the pendulum having a velocity of 3.8 m/s at room temperature

3.6 Fourier transform infrared spectroscopy(FT-IR)

The surface chemistries of composites were evaluated using a Thermo Scientific Nicolet IS 10 FT-IR spectroscopy. Attenuated total reflectance method was used to collect IR spectra. All data was recorded at room temperature in the spectral range 450 – 4000 cm^{-1} with a signal resolution of 4 cm^{-1}. For pure LDPE matrix and composite materials, carbonyl index of composites were calculated from Equation 3.1.

$$\text{Carbonyl Index} = \frac{I_{1712}}{I_{2915}} \quad \textbf{(3.1)}$$

3.7 Differential scanning calorimetry(DSC)

The thermal properties of the stabilized and unstabilized composites was studied by differential scanning calorimetry analysis. DSC analysis of the specimens was performed using a Perkin – Elmer 4000 differential scanning calorimeter with temperatures ranging from -80 to 250 ˚C with a heating rate of 10 ˚C/min in nitrogen (flow rate 20 mL/min) by using samples which have weights of approximately 4–8 mg. Samples were held in a platinum crucible. The degree of crystallinity of all composites was determined from the DSC analysis using the Equation 3.2 :

$$\% \text{ Crystallinity} = \frac{\Delta H}{\Delta H_m} \times \frac{100}{W} \quad \textbf{(3.2)}$$

Where ΔH and ΔH_m are the heat of fusion of LDPE and 100% crystalline LDPE, respectively, and W is the fraction of LDPE in composites. Taking ΔH_m=293J/g. for LDPE, the crystallinity of LDPE in composites was calculated.

3.8 Colorimetric analysis

Color measurements were performed in accordance with ASTM 2244 using a Data Color 3890 spectrophotometer measures the color L*a*b* coordinates. L* represents the lightness coordinate and varies from 100 (white) to 0 (grey); a* represents the red (+a*) to green (−a*) coordinate; b* represents the yellow (+b*) to blue (−b*) coordinate. At least five replicates were measured to obtain the average values of color. In order to determine the discoloration (ΔE) of the weathered samples, the following Equation 3.3 was used :

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad \textbf{(3.3)}$$

with ΔL*, Δa* and Δb* as the difference of initial and final values of L*, a* and b* for all composites materials.

4. RESULTS AND DISCUSSION

4.1 Mechanical Properties

Mechanical properties of unstabilized and stabilized composites are shown in the Table 4.1. The results for unweathered composites showed that adding HALS (1%wt) did not greatly influence the tensile strength of composites but did improve the modulus of elasticity about 15%. An increase in MOE of CF/LDPE stabilized with HALS (1%wt) composites decreased the strain at break value about 23%. The TS of CF/LDPE composites stabilized with UVA in both ratios also were found to be improved but the modulus of elasticity increased by adding UVA (0.2%wt) only about 3%. Adding antioxidant with AOx (0.5%), the modulus of elasticity was increased about 20% while the tensile strength was increased 2.5% compared with the unstabilized composite. Significant changes were observed at all ratios of other additives.

A significant increase in the modulus of elasticity was observed in the 120 h of weathering which is approximately 11% due to the photo-degradation of LDPE matrix. After 120 h UV exposure, modulus of elasticity was observed to increase continuously with the further UV weathering up to 240 h. This behavior of unstabilized CF/LDPE was not expected. This can be explained by the interfacial adhesion between LDPE matrix and cotton fiber. It is possible that interfacial adhesion can be enhanced by photodegradation which creates carbonyl groups in LDPE matrix. These groups are more compatible with the cellulose in the cotton fiber structure, causing the increment in modulus of elasticity behaviour. Abu-Sharkh and Hamid et al [56] indicated that interfacial adhesion between PP and fiber can be improved by degradation and it causes the increase of strain at break properties of composites. It was also reported that the composites may be broken at the interface between polymer and fiber, which is the weakest point in the composites. Also, the effect of weathering on the strain at break can be shown in the Figure 4.3. As we

expected, the strain at break which is called deformability of composites, decreased upon increasing UV exposure time. It is shown that the initial strain at break of CF/LDPE composite is nearly 10%. However, the CF/LDPE composite became very brittle after exposure time. This is a consequence of the large drop in molecular weight associated with degradation. The CF/LDPE composite showed the largest drop than the stabilized composites in strain at break which is nearly 20%. Also, the tensile strength of the unstabilized composites decreased nearly 25% after 240 h of exposure.

Table 4.1 : Mechanical property values of stabilized and unstabilized CF/LDPE composites

Samples	Exposion Time(h)	Tensile strength (MPa)	Modulus of Elasticity (MPa)	Strain at break (%)
CF/LDPE	0	18.83	933.09	10.46
	120	16.62	1035.63	9.54
	240	13.97	1055.42	8.41
CF/LDPE/HALS(0.5%)	0	19.48	974.78	12.91
	120	18.37	922.26	11.78
	240	17.81	948.83	10.87
CF/LDPE/HALS(1%)	0	18.62	1076.56	9.67
	120	16.51	904.15	9.02
	240	15.35	994.15	8.65
CF/LDPE/UVA(0.2%)	0	19.16	955.56	9.01
	120	15.23	1010.47	8.87
	240	15.08	919.32	8.12
CF/LDPE/UVA(0.4%)	0	19.17	901.11	12.67
	120	15.48	995.26	11.47
	240	14.51	938.48	11.02
CF/LDPE/AOx(0.5%)	0	19.31	1125.91	10.3
	120	16.63	997.99	9.94
	240	14.75	954.75	10.4
CF/LDPE/AOx(1%)	0	18.91	910.17	10.95
	120	17.3	915.23	10.2
	240	15.3	965.47	9.74

The mechanical properties vary according to the UV additives and their ratios for stabilized composites. Figure 4.1 represents to the change in tensile strength for all composite materials. According to these results, the CF/LFPE composite stabilized

with especially HALS (0.5%wt) showed the best result to protect the tensile strength property of CF/LDPE composites and also retarded the degradation of composites against the UV radiation. It can be seen that tensile strength dropped by approximately 8% from 19.48MPa to 17.81MPa. UV absorbers also effected positively to the mechanical properties of CF/LDPE composites. The tensile strength of CF/LDPE/UVA (0.2%) composite decreased approximately 21% during the 120h UV weathering. However, no significant reduction observed after 120h. For example, the CF/LDPE composites stabilized with UVA (0.2%) have the tensile strength reduction 20.5% and 21.3% for 120h and 240h, respectively. The explanation can be easily found considering that stabilized composites efficiency can be appeared with increasing the exposure time. Also, composites stabilized with AOx in the composite materials decreased nearly 19%. It was seen that there is no significant effect on tensile strength property by using the antioxidants.

Figure 4.1 shows that the change in modulus of elasticity of all composites. It can be seen that the modulus of elasticity value of HALS did not show the same trend as it was expected. Almost no change was observed in the CF/LDPE/HALS (1%) composites. Adding UVA with both ration into the CF/LDPE composites caused the increment to the modulus of elasticity during 120h of weathering, as we expected. This increase can be a sign of an increase in crystallinity. Stark and Matuana et al. [12] reported that the flexural modulus increased because of the increment in crystallization of HDPE. Between 120h and 240h of weathering, the CF/LDPE stabilized composites with UVA (0.2 and 0.4%) also experienced a drop in MOE. However, the loss in MOE was 9% for stabilized with UVA (0.2%) and only %4 for stabilized with UVA (0.4%). That means, the photostabilizer UVA (0.4%) clearly prevented some loss in MOE of the CF/LDPE composites after weathering. The CF/LDPE stabilized with AOx (1%) increased approximetly 6% which is the highest value among the all stabilized composites. The modulus of elasticity increased with increasing exposure time because the rigidity of composites increases which effects the chain scission reactions in photodegradation mechanism.

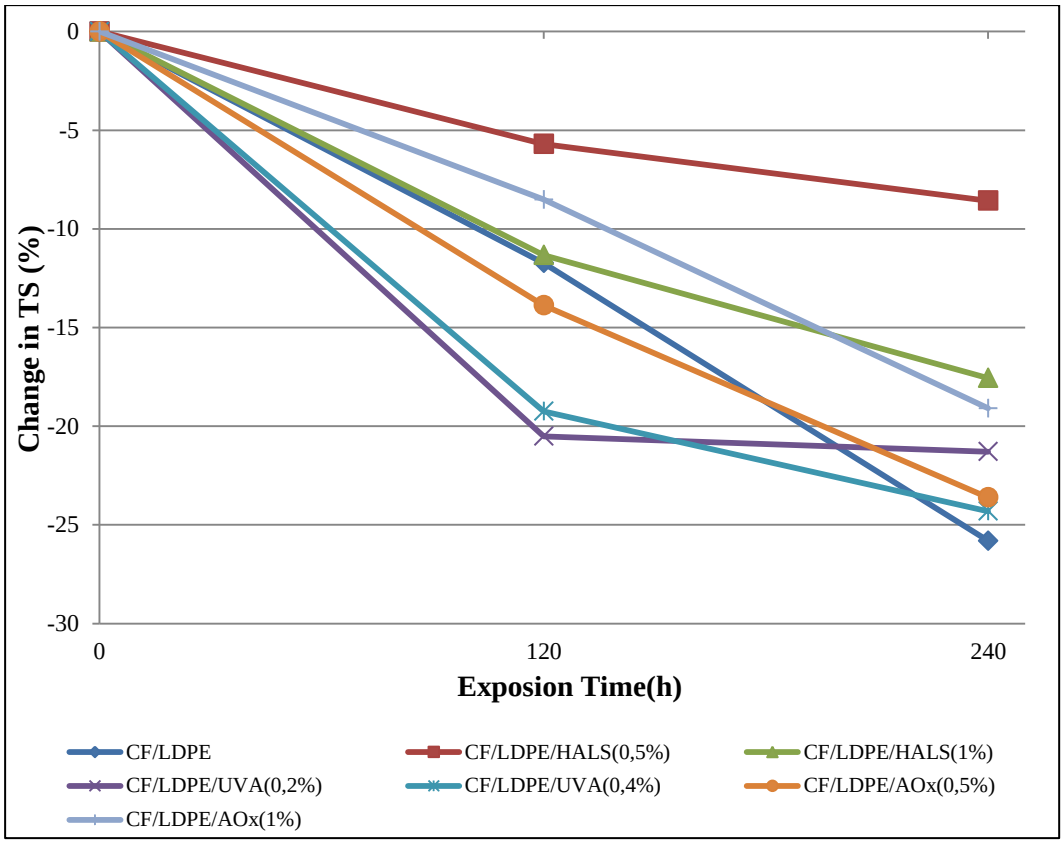


Figure 4.1 : Change in tensile strength as a function of exposure time for all CF/LDPE composites.

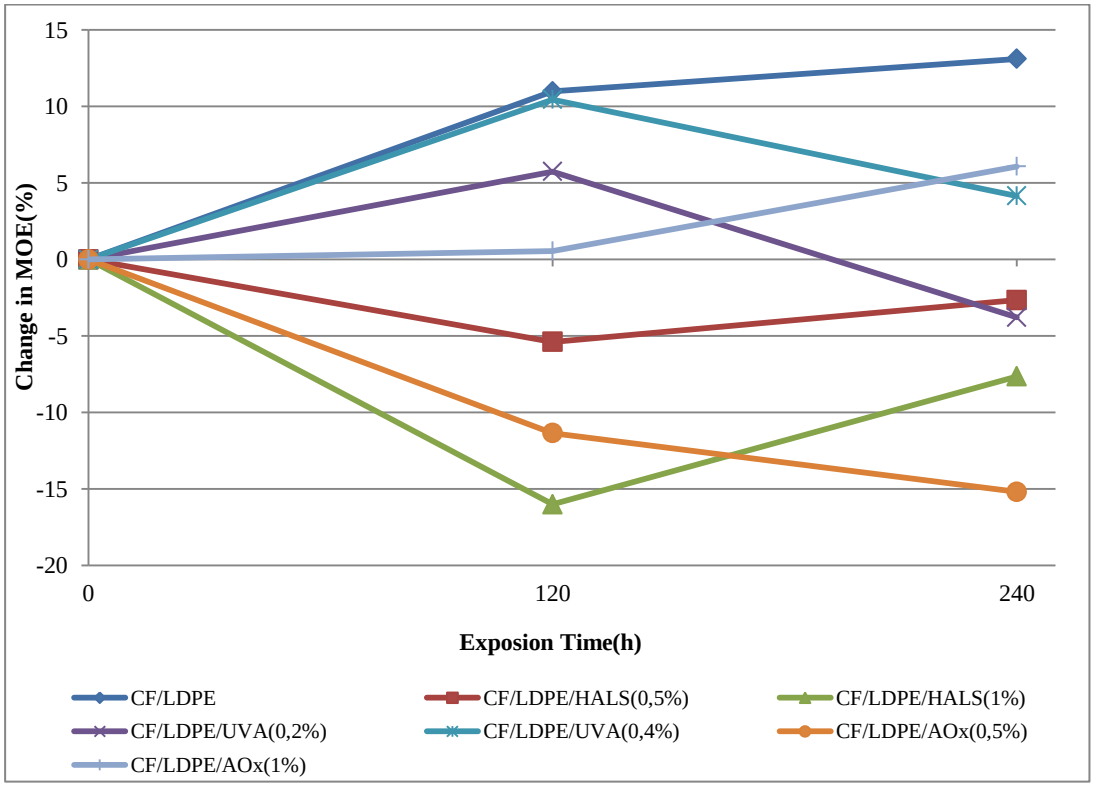


Figure 4.2 : Change in modulus of elasticity as a function of exposure time for all CF/L9DPE composites

Figure 4.3 represents the change in strain at break property of CF/LDPE composites. The ultimate strain at break of the unstabilized CF/LDPE composite material is much lower than stabilized composites. This is a much lower ductility of the composites[56]. For unstabilized composite, the strain at break dropped by 1% from 10.95 to 9.74, showed the highest value than the stabilized composites. Among the stabilized composites, UVA (0.2), HALS (1%) and AOx (0.5%) showed the best results for strain at break property.

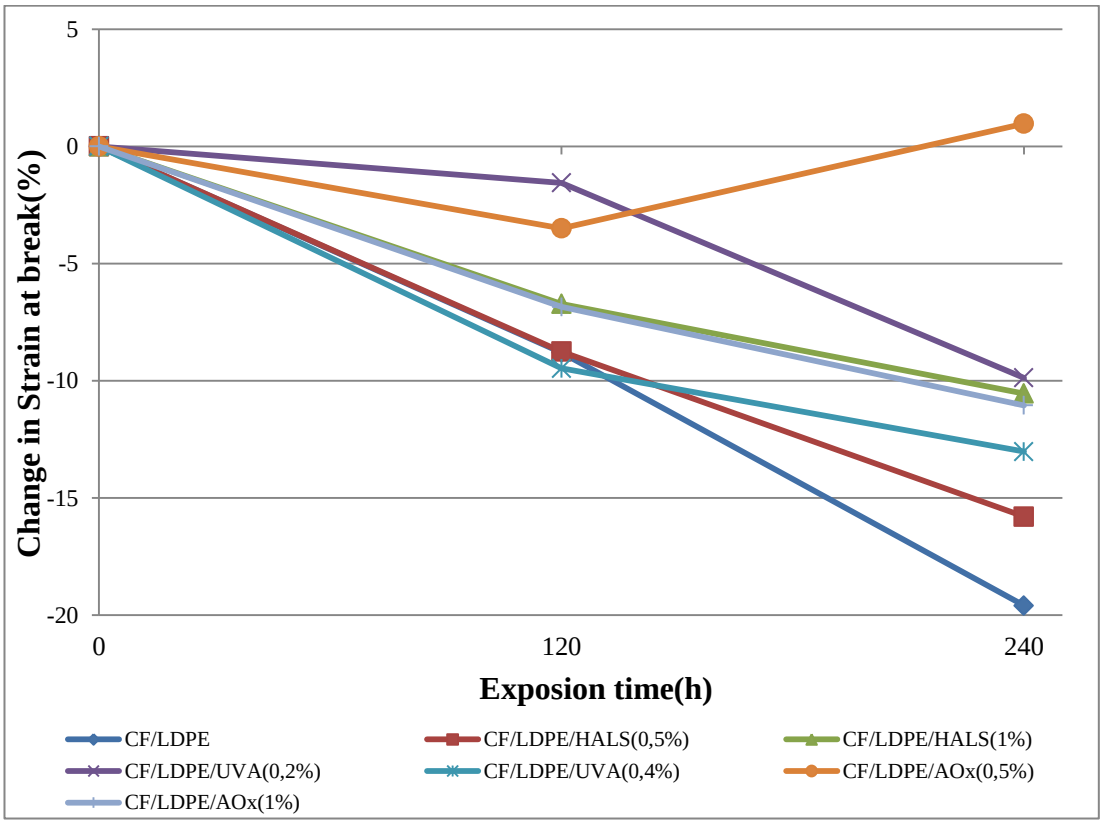


Figure 4.3 : Change in elongation at break as a function of exposure time for all CF/LDPE composites

Generally, CF/LDPE stabilized with HALS has the better tensile strength properties than the other stabilized composites after 240h of weathering. It can be seen that using antioxidant and UV absorbant effected the tensile properties of composites approximately 10-12% and 12-14%, respectively. However, the stabilized samples did not show the same trend in modulus of elasticity and strain at break properties.

Figure 4.4 showes the change of impact strength properties of unstabilized and stabilized composites. During the first 120h of weathering, it cannot be seen significant change for unstabilized CF/LDPE composites. In fact, within 240h of exposure, almost 12% of the value of this property was lost. The main reason of this lost can be explained by photodegradation mechanism of composites and formation of microcracks in the composite surface. The presence of UV additives in the composite structure reduced significantly the rate of decline of the impact strength. Adding HALS (0.5%) to the CF/LDPE composites did not show distinctive effect during exposure, while adding HALS (1%) decreased the impact strength nearly 4% during 240h of exposure. Also UVA (0.4%) and AOx (0.5% and 1%) decreased the impact strength approximately 6-7% during exposure time. However, there is no significant effect on the impact strength of composites stabilized with UVA (0.2%).

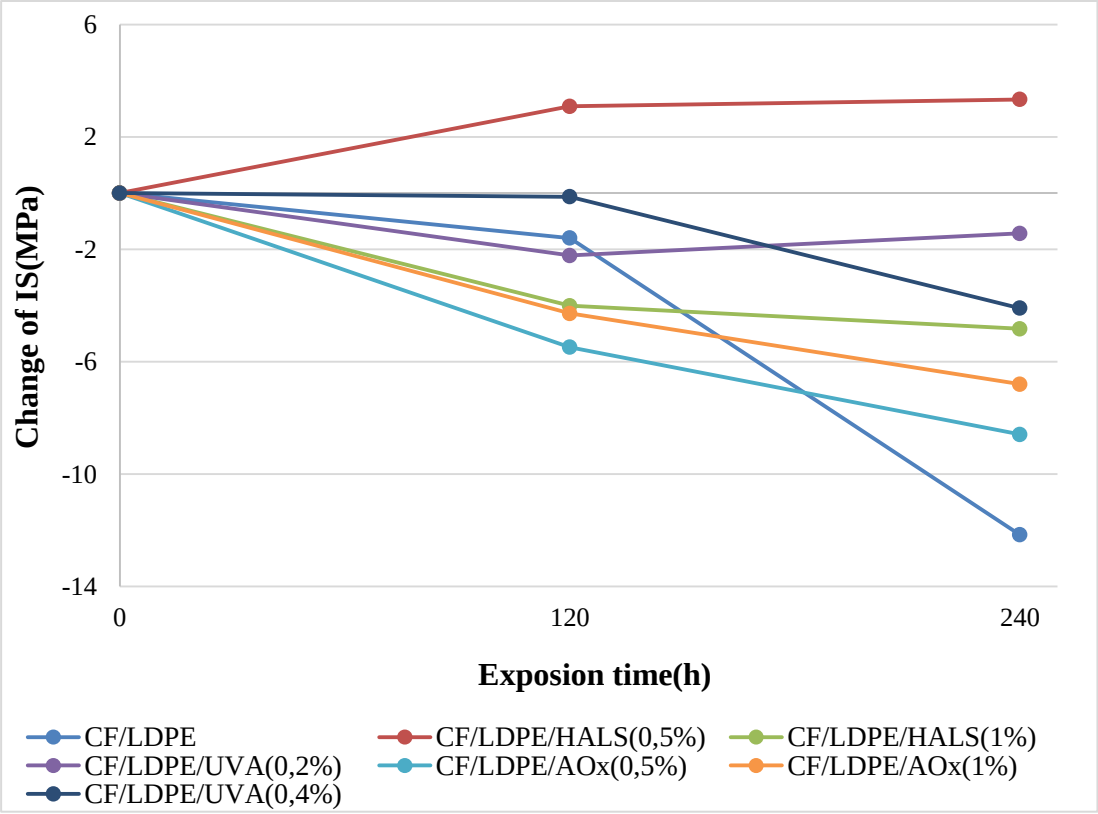


Figure 4.4 : Change in impact strength as a function of exposure time for all CF/LDPE composites

Finally, with regard to the general mechanical properties of CF/LDPE composites, the above results suggest the best results obtained from CF/LDPE composites

stabilized with HALS (Chimmasorb) continuing to this line: HALS>UVA>AOx>Unstabilized.

4.2 Thermal properties

The DSC curves obtained for unstabilized composites exposed to accelerated weathering are shown in Figure 4.5. Also, Figure 4.6 shows that the crystallinity values for CF/LDPE and stabilized CF/LDPE composites. Crystallinity values were calculated from the Equation 3.2.

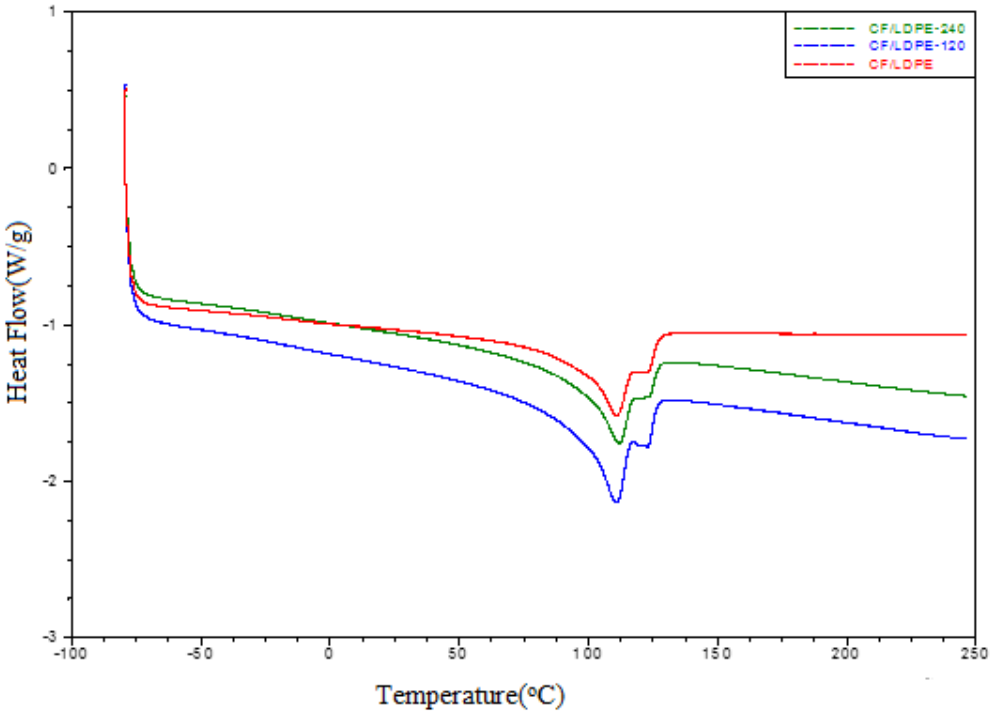


Figure 4.5 : DSC diagram for unstabilized CF/LDPE composite

In the unstabilized CF/LDPE composites, the crystallinity of the samples increased through 120 hours of exposure. An increase in crystallinity can be used as an indicator of polyethylene chain scission during photodegradation. In the two photodegradation mechanism (Norrish I and II), chain scission and crosslinking compete during the weathering process. Chain scissions reduce the density of the entanglements in the amorphous phase, allowing shorter molecules to crystallize because of their higher mobility. Then, they can undergo recrystallization and result in an increase in crystallization. After 120h of exposure, the crystallinity value of unstabilized CF/LDPE significantly decreased. We expected that the crystallinity

would increase, because chain scission occurs during exposure as evidenced by the growth of carbonyl groups. However, the crystallinity values decreased after 120h of weathering due to damaging to the tie molecules. Tie molecules are formed a part of a folded crystalline region and extend through an amorphous region into another crystalline region. Zoe et al reported that as the chain scission was proceeding, the tie molecules can be exposed to damage due to the oxidation. Thus, tie molecule fragmentation led to decrease in crystallinity[14]. Therefore, the crystallinity value of CF/LDPE composites increased by 12% from 38.6 to 43.2 during 120h of exposure and then a significant drop in crystallinity observed in the unstabilized composites. An approximately 25% drop from the initial value corresponded to the formation of surface cracks.

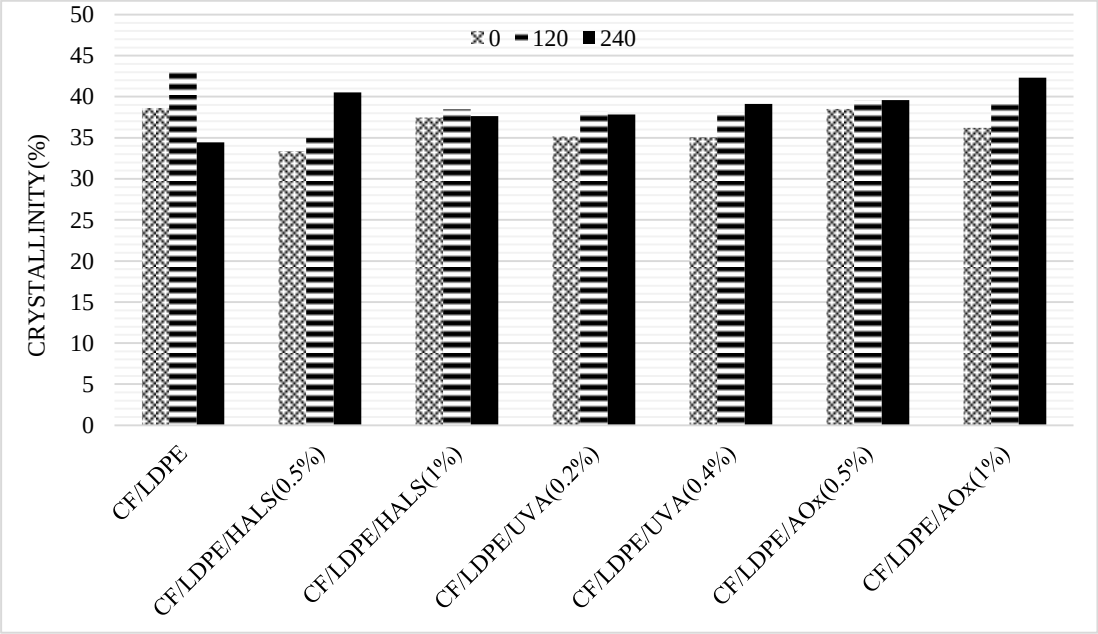


Figure 4.6 : Crystallinity values of stabilized and unstabilized CF/LDPE composites

Although UV stabilizers were used in the CF/LDPE composites, the crsytallinity increased after 120h of weathering. According to the Stark and Matuana, the increment of the crystallinity values for stabilized composites may be evidence for formation of chain scission in CF/LDPE stabilized composites[35]. After 240h of exposure, the net crystallinity values for CF/LDPE stabilized composites with HALS (0.5%), UVA (0.4%) and AOx (1%) continuously increased. However, the net change in crystallinity for CF/LDPE stabilized composites with HALS (1%), UVA (0.2%) and AOx (0.5%) was not significant. These results confirm that the stabilizers

have the ability to delay chain scission. Kaci et al. used FTIR and DSC to determine the crystallinity of low density polyethylene stabilized with HALS after natural weathering[57]. In this study, the crystallinity increased with an increase in exposure time until a plateau was reached after 400 days.

For stabilized with HALS (1%) and AOx (0.5%), the crystallinity increased nearly 3% during 120h of exposure. However, between 120h and 240h of exposure, there were not observed a significant change in crystallinity values of CF/LDPE/HALS (1%) and CF/LDPE/AOx (1%). This result is the evidence to delay some chain scission[35].

4.3 Surface analysis

FTIR spectroscopy was used to determine structural changes in the surface chemistry of stabilized and unstabilized CF/LDPE composites during accelerated weathering. Table 4.2 shows the most significant bands in the infrared spectra of the composites, and distinctive functional groups. As can be seen in Figure 4.7 in the FTIR spectra for the surface layer of the studied composites, a number of bands were related to both cotton and polyethylene. Some characteristic bands, such as 2916cm^{-1} for polyethylene and 1510cm^{-1} for the lignin component of cotton were found in the FTIR spectra of the surface layer of the composites. Also, Figure 4.8 represents to the carbonyl index for all composite materials.

Table 4.2 : Wavenumbers of peaks used for FTIR analysis and corresponding vibrational types[a]

Wavenumber (cm-1)	Assignments
3244	O-H stretching (hydrogen bonded)
2915	C-H stretching in methyl and methylene groups
1712	C=O stretching
1472	C-H bending, crystalline
1462	C-H bending, amorphous
1170	C-O stretching
730	C-H rocking, crystalline
720	C-H rocking, amorphous

[a]Sources: Ref. [12, 58-60]

In the unweathered composites, the carbonyl index is observed for unstabilized and stabilized CF/LDPE composites because of chemical structure of hemicellulose and lignin[61]. Sahar Al-Malaika et al said that low density polyethylene undergoes

molecular entanglement in the presence of excess oxygen during processing stages. Alkyl and alkoxyl radicals which composed in the polymer backbone chain are ultimately responsible for the formation of carbonyl groups due to the UV radiation. Also, in the initial stage of processing, all thermoplastic polymers show a high rate of mechanical degradation. This degradation causes the introduction a variety of irregularities into the macromolecule and this is shown to have a profound effect on the following aging performance of the polymer [51]. In CF/LDPE composites, the radicals composed of extrusion and breakage process have more domains due to the addition of photostabilizers. Therefore, the carbonyl index values was seen higher in the unweathered composites. Also, the carbonyl index value of antioxidant adding composites is higher than the carbonyl index of other composites. This excess carbonyl groups come from the chemical structure of antioxidant (Figure 4.8).

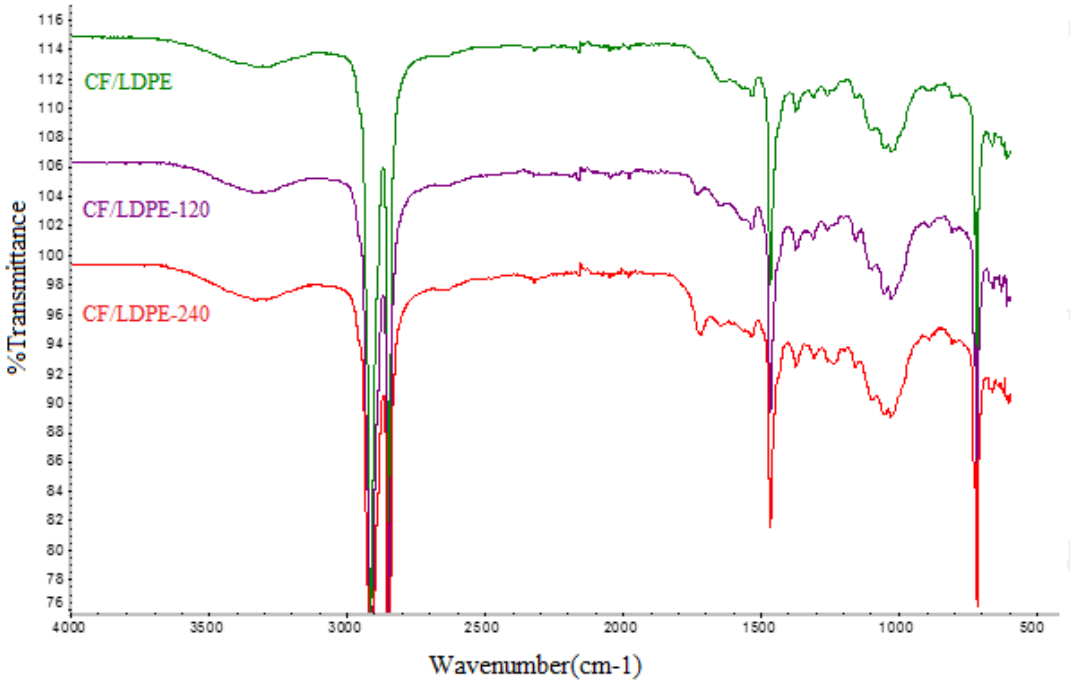


Figure 4.7 : FTIR diagram of unstabilized (CF/LDPE) composites

For unstabilized composites, the carbonyl index increased approximately 2% in the first 120h of exposure. During this exposure, it was not observed significant effect for stabilized with AOx (0.5%). After 120h of exposure, the carbonyl index continued to increase, nearly 3% for unstabilized composites. It is known that the increment in the carbonyl index indicates severe photo-oxidative reactions in the CF/LDPE composites [53]. Therefore, the results show that chain scission may have occurred immediately upon UV exposure and that the number of chain scissions

increased with increasing exposure time. However, the increment of stabilized composites was less than of the unstabilized composites. Totally, the most increament was observed nearly 5% for only unstabilized composites. After 240 of exposure, the HALS (5%) and HALS(1%) exhibited the decrease in the carbonyl index. Especially HALS (1%) decreased approximetly 1% after 240h of exposure. This result indicate that HALS (1%) was more effective than the other stabilized composites due to the primary function of radical scavenger.

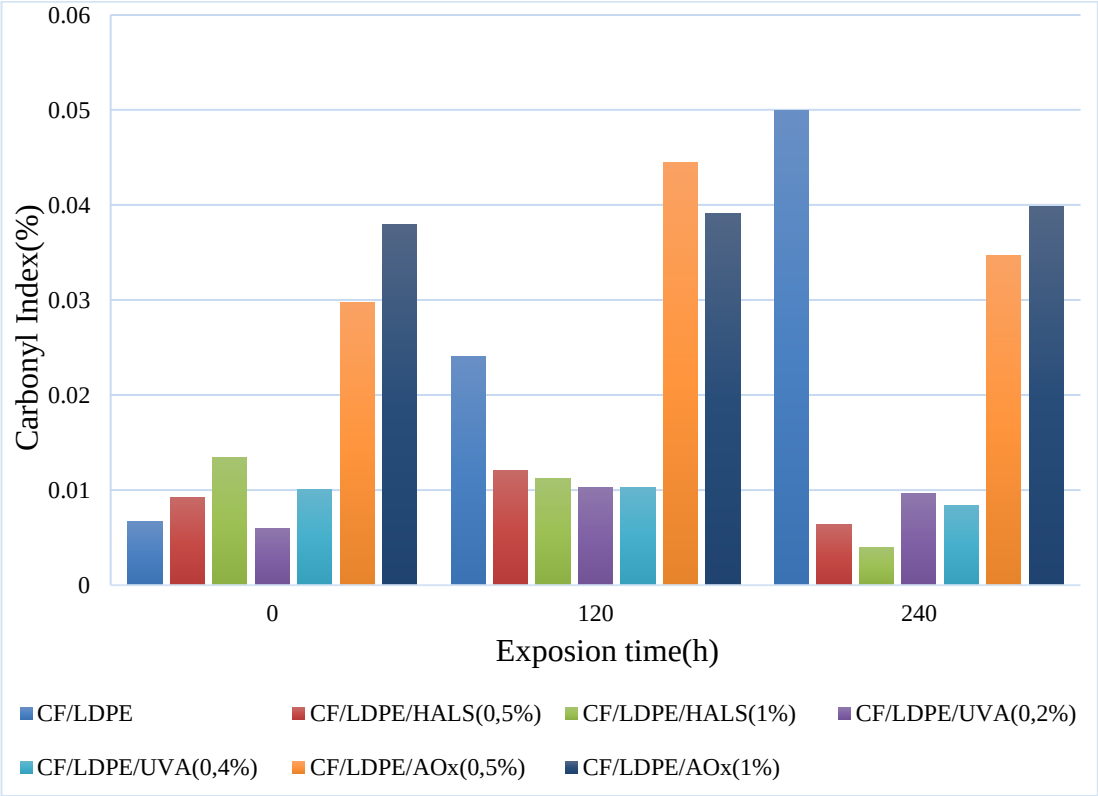


Figure 4.8 : Carbonyl index of all composites

Figure 4.9 and 4.10 show that HALS offers significant protection to the CF/LDPE composites by lowering the photo-oxidative mechanism which is responsible for the formation of ketone groups. This suggestion was reported by Kaci et al [33]. They reported that the ketonic carbonyl formed their photochemical reactions (Norrish I and II) with radical or molecular species present in the polyolefins during the oxidative degradation deactivate by hindered amine light stabilizers in LDPE. Therefore, the carbonyl concentration during all exposure time can be attributed to the deactivation of ketonic carbonyls in LDPE by HALS.

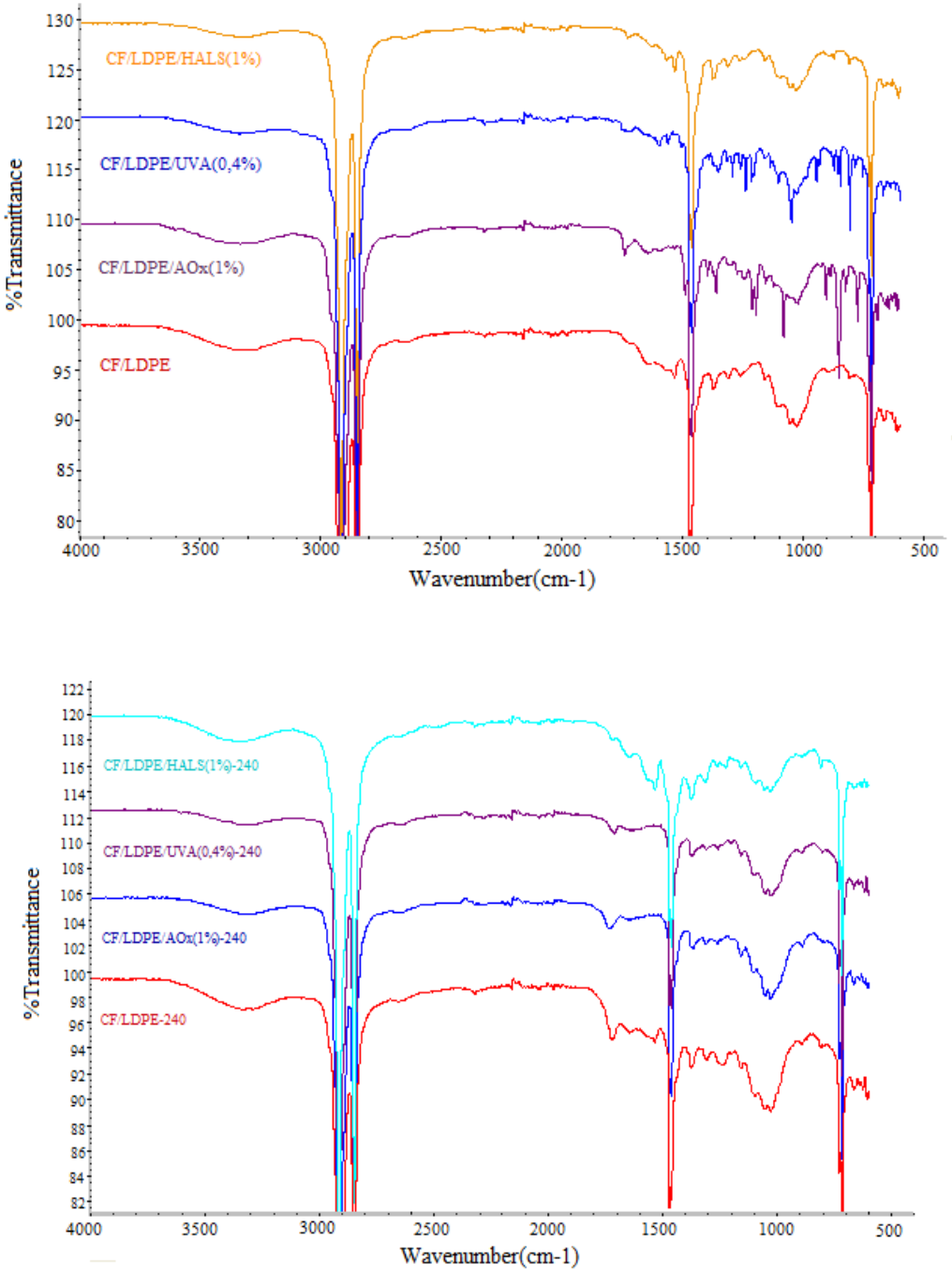


Figure 4.9 : FTIR diagram of unexposed and 240h of exposed composites.

Our results indicate that there is no effect on the carbonyl index of CF/LDPE composites when the composites are stabilized with AOx, as we expected. The antioxidant which is Irganox 1010 is the type of chain-breaking donor (CB-D) (hindered phenols) (Figure2.12) and they are generally less effective than chain-breaking acceptor (CB-A) antioxidants. However, they are still used for stabilization because they are cheap and non-discoloring additives [58].

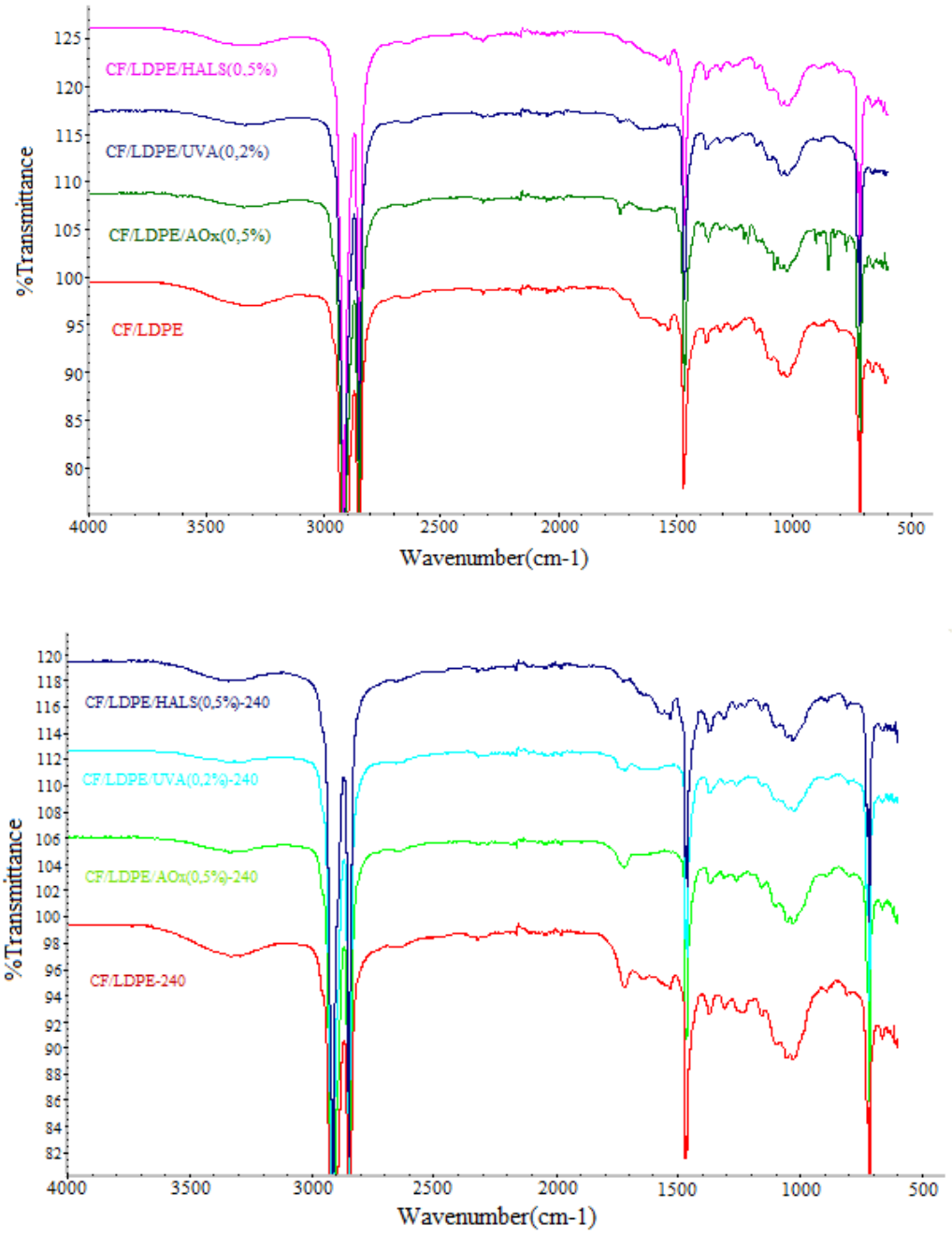


Figure 4.10 : FTIR diagram of unexposed and exposed composites

4.4 Color analysis

Color analysis were performed for unstabilized and stabilized CF/LDPE composites exposed UV radiation for a total of 240h in accelerated weathering. The effect of accelerated weathering on the composites color change is shown in Figure 4.11, Figure 4.12, Figure 4.13, and Figure 4.14. The lightness (L*) and chromacity coordinates (a* and b*) were measured. The positive ΔL* increment represents the

lightening of composites and the negative ΔL* increment the darkening (fading) of composites. The coordinates of a* and b* values represent the red-green and yellow-blue direction, respectively. Also color change (ΔE*) were calculated by using Equation 3.3.

Adding fiber into the polymeric composite materials delayed to the degradation of polymer matrix during UV exposure because of the lignin property. Lignin which is present at the structure of fiber acts as a natural antioxidant. Abu-Shark and Hamid et al. reported that lignin is known to stabilize the natural fiber due to the role of the lignin. It is known to stabilize the natural fiber because it acts as a natural antioxidants. The samples discolor and become brownish when the natural fiber is used in the processing into the composites. The surface layer of fiber can also act as a protective layer which prevents UV exposure from penetrating the polymeric matrix and causing degradation in the bulk[56]. Thus, the degradation of lignin is important for the color measurement of CF/LDPE composites.

Figure 4.11 shows that the Δa* value of CF/LDPE and stabilized CF/LDPE composites. The a* value of all composites decreased at the same rate during 120h of exposure. However, after 120h, a significant change was not observed. Also, Figure 4.12 shows that the Δb* values of CF/LDPE composites. The b* values displayed the same trend for all of the CF/LDPE composites. The Δb* value of CF/LDPE composite which indicates the yellowing of samples decreased significantly after 240h of exposure. That means chromophores undergo degradation which leads to the photo-bleaching. Muasher and Sain et al explained the decrease with the redox reaction of lignin (Figure2.7). They said that the redox reaction of the hydroquinone and paraquinone structur.es are supported the Δb* behavior. The reaction begins with the oxidation of the hydroquinones to form paraquinones (chromophoric structures) under UV exposure. Chromophoric groups such as carboxylic acid, quinones and hydroperoxy radicals are the main cause for discoloration, mainly yellowing the fiber. Moreover, the reduction of the paraquinone to hydroquinone groups which causes to photobleaching may be lead to decrease in yellowing with increasing exposure time. The reaction from paraquinone to hydroquinone is undesirable formation due to the ability to oxidize again and remake paraquinone that reinitiate the redox reaction[2]. Thus, the maximum negative value of unstabilized CF/LDPE indicated that they affected more from the lignin photodegradation reaction.

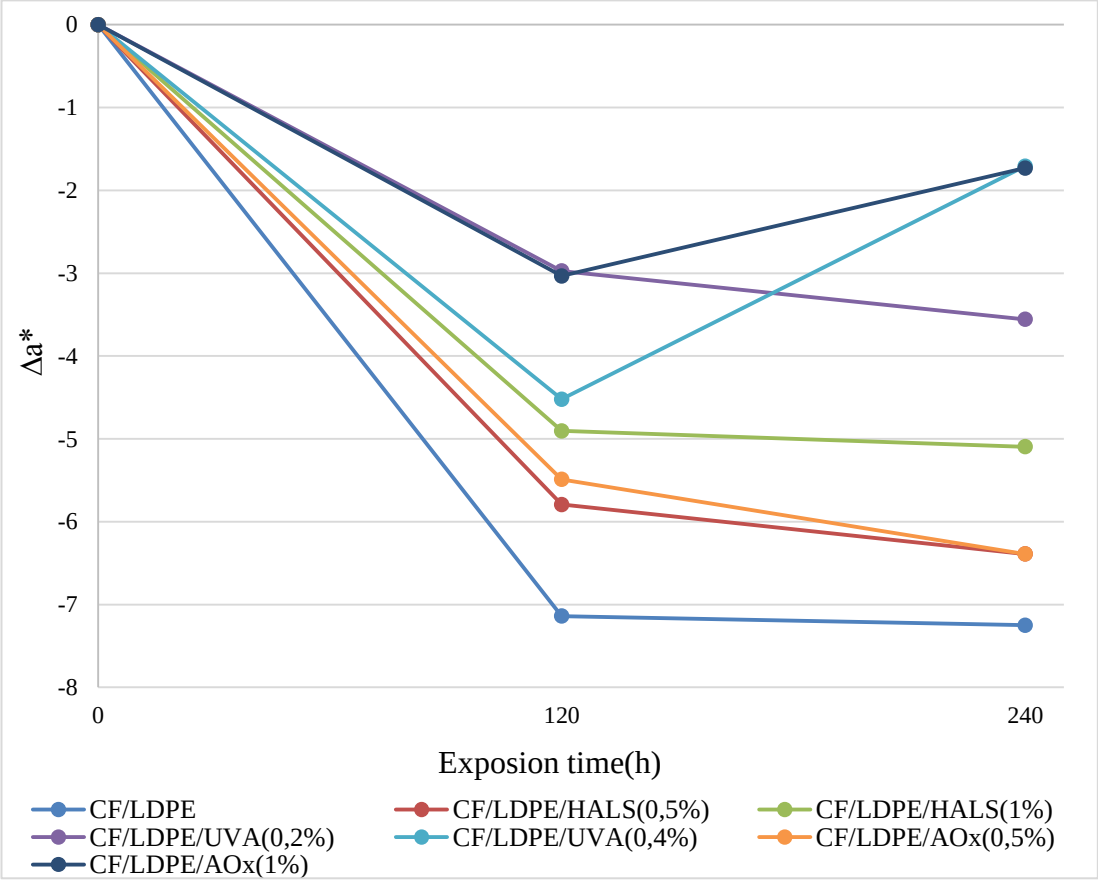


Figure 4.11 : Δa* values of unstabilized and stabilized composites

All of the stabilized composites exhibited a decrease in the Δb* which elucidates to a decrease in chromophoric formation[34]. HALS stabilized composites exhibited the most negative change in the Δb* value among the all stabilized composites after 240h of exposure. As can be observed in Figure 4.12, Δb* values of CF/LDPE and CF/LDPE/HALS (0.5%) were nearly same. Also, the total decrase of Δb* value for CF/LDPE/HALS (1%) was close to the unstabilized composites. This decrease indicates its ability to continue to scavenge free radicals and increase the formation of hydroquinones. Figure 4.9 exhibits a decrease in the carbonyl absorbance at 1724cm^{-1} with increasing exposure time which indicates to the formation of hydroquinones. The addition of UV absorbers to the CF/LDPE composites resulted in retention of photobleaching. Hua Du et al. UV absorber are more effective than the HALS, regardless of molecular weigth. They reported that UV absorbers absorb UV radiation before fiber is exposed and bleached. Thus, after 240h of UV exposure,

the addition of both content UV absorbers prevented further photobleaching of composites[54]. Figure 4.12 shows that the least change in photobleacing was in composites stabilized with AOx. The effect of chain-breaking antioxidants as a photostabilizer is small but some of their oxidative transformation products are photosensitizing. They are also called non-discoloring additives [51].

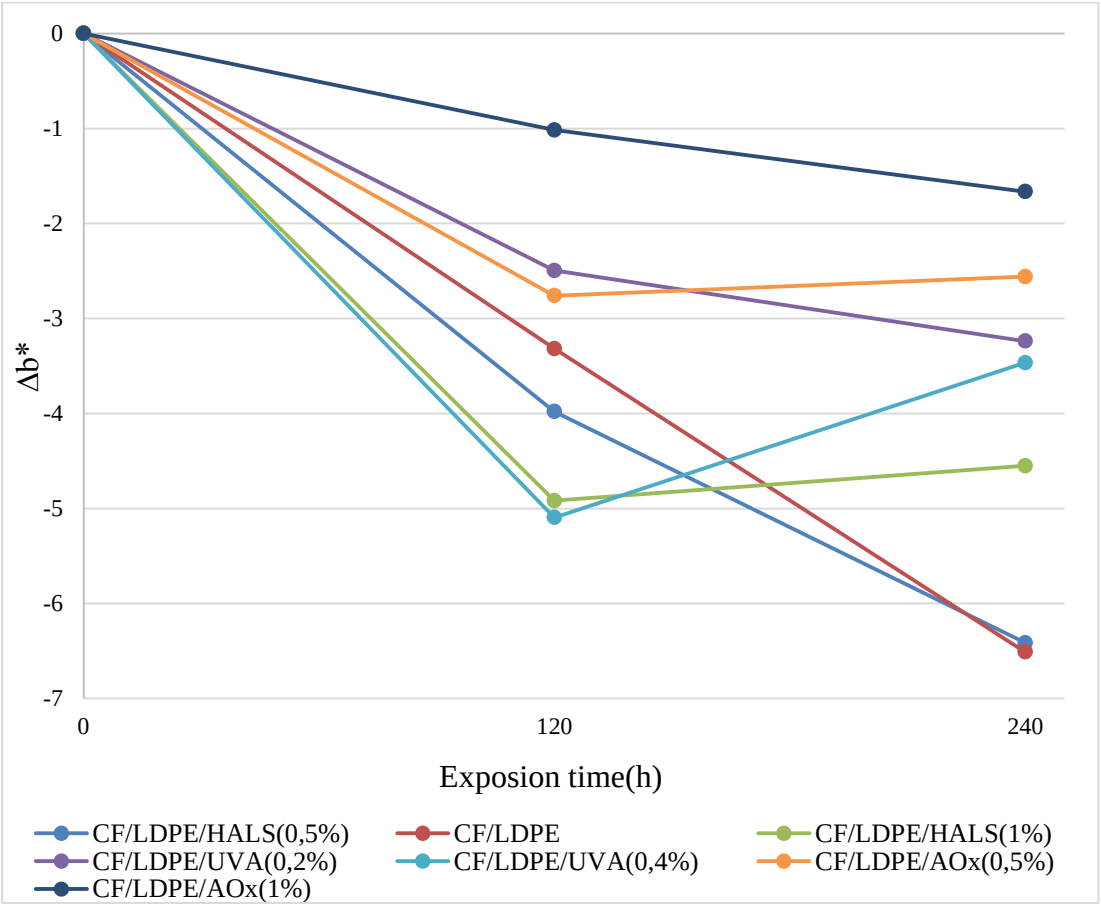


Figure 4.12 : Δb* values of unstabilized and stabilized composites

Figure 4.13 shows the change in the ΔL* value with exposure time for unstabilized and stabilized CF/LDPE composites. From this figure, it is observed that the lightness factor (ΔL*) increased for all composites after 240h of exposure. The increase in the ΔL* value may be attributed in part to the chain scission of LDPE and its migration to the surface and in another part to the photobleaching of lignin. The possibility was stated that lignin in the composites generated radicals during photooxidation which attacked the LDPE chains[62]. After 240h of exposure, most

of the stabilized CF/LDPE composites ΔL* values were lower than the unstabilized composite.

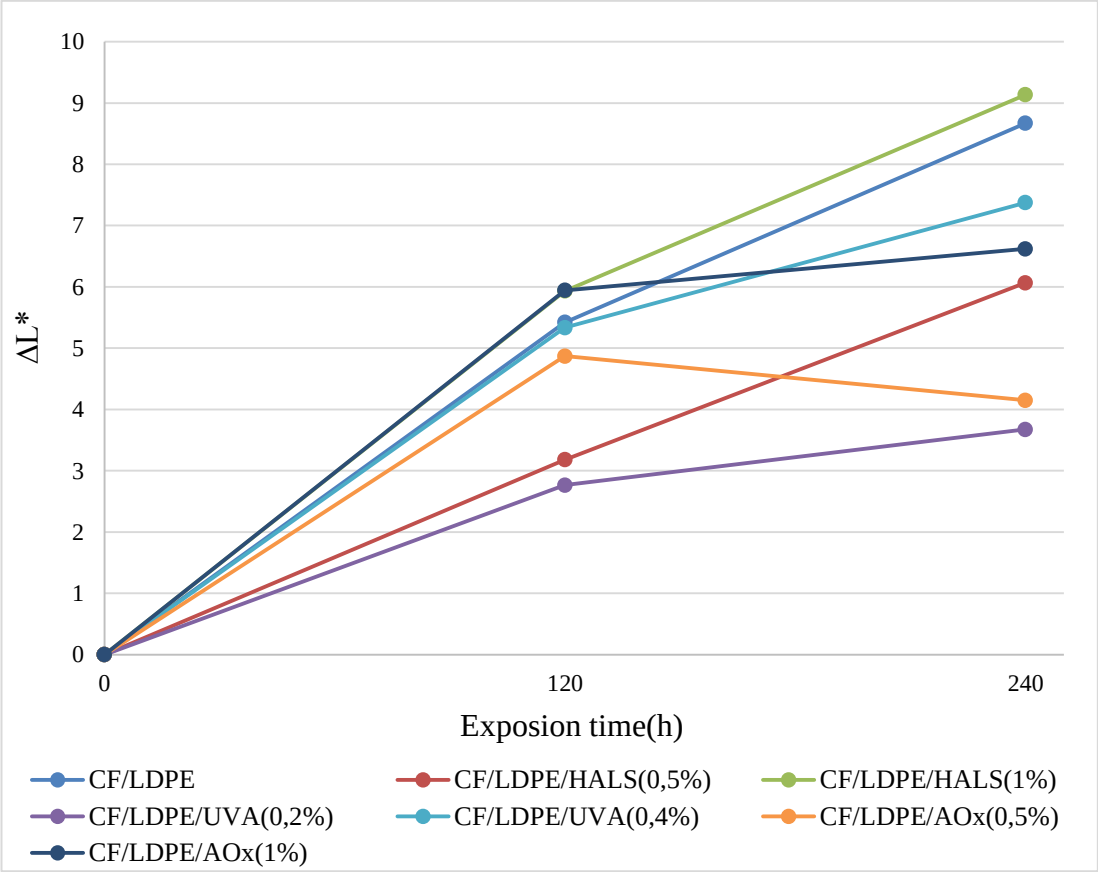


Figure 4.13 : ΔL* values of unstabilized and stabilized composites

When comparing the effectiveness of CF/LDPE/UVA(0.2%) versus CF/LDPE/HALS (0.5%) on controlling lightning, Figure 4.13 shows that rate of increase ΔL* value is comparable for in the second 120h of exposure. However, the ΔL* value for CF/LDPE/HALS (0.5%) continued to increase significantly after the first 120h while CF/LDPE/UVA (0.2%) increased at a much slower rate. In this study, it was assumed that UVA could inhibit lightening by absorbing UV radiation; this resulted in less UV radiation being available to bleach the samples. The ΔL* values of stabilized with HALS (1%) and AOx (1%) composites increased at the same rate in the first 120h. A little change was observed for CF/LDPE/AOx (1%) between 120h and 240h of exposure whereas the ΔL* value of CF/LDPE/HALS

(1%) continued to increase. In this was, it may be proposed that the AOx (1%) is more effective than HALS (1%) on color fading.

A general conclusion that can be drawn after analysis of color change is that stabilized composites showed lower total change compared to the unstabilized composites (Figure 4.14). The total discoloration of CF/LDPE/UVA (0.2%) increased at least after 240h of exposure while the CF/LDPE/HALS (1%) has the highest ΔE* value along the stabilized composites. In this study, it can be proposed that UV absorbers were considerably efficient to inhibit discoloration by absorbing UV radiation.

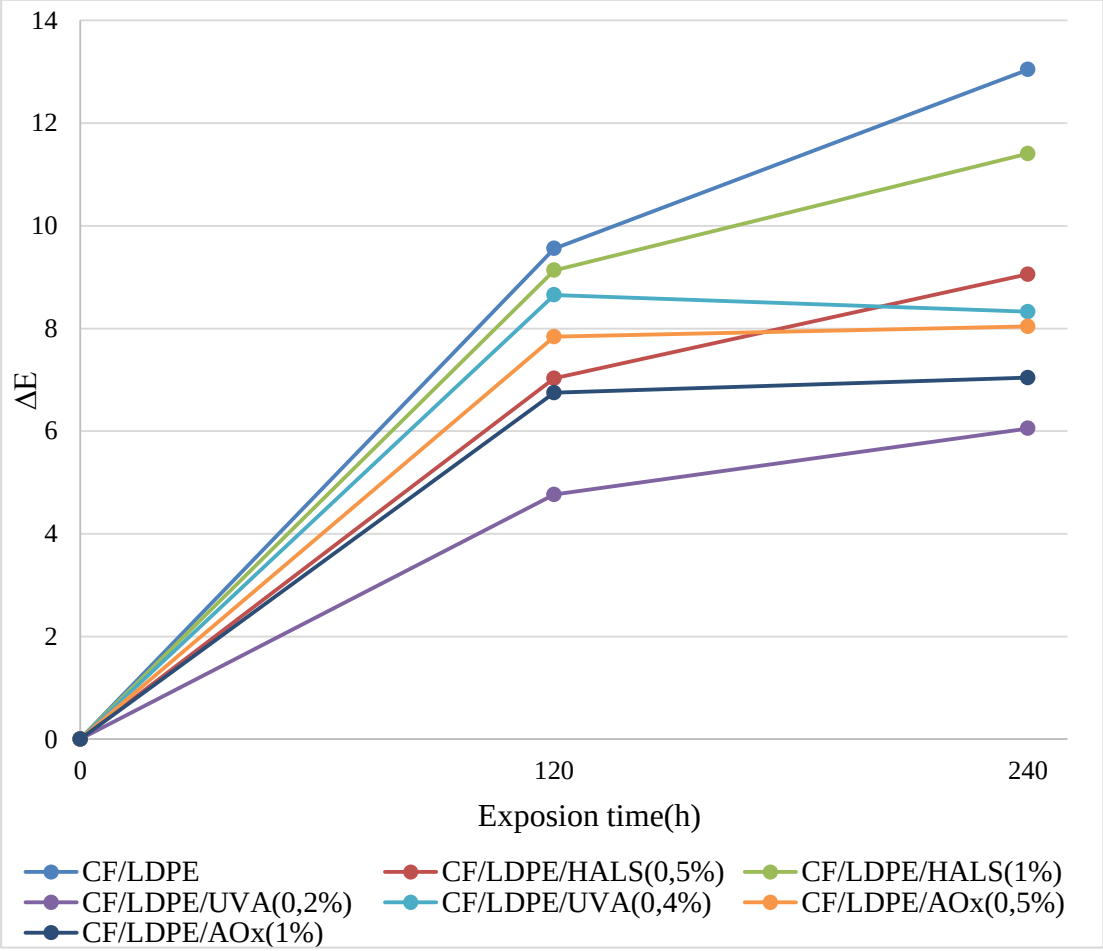


Figure 4.14 : ΔE values of unstabilized and stabilized composites

5. CONCLUSION

The aim of this study is to manufacture UV stabilize cotton fiber low density polyethylene composites. In this study, ultraviolet absorber (UVA), hindered amine light stabilizer (HALS) and antioxidant (AOx) were used to delay or minimize the effect of UV exposure in the CF/LDPE composites. They were manufactured by using a custom made single screw extruder. Then, the CF/LDPE composites were pressed to maintain constant thickness and flatness. Composites were cut out by using a desktop CNC milling machine for tensile and impact testing. Cotton fiber low density polyethylene composites were exposed to both Ultraviolet (UV) light exposure for the time periods of up to 240h. These results were found after 240h of weathering:

1. Mechanical properties were investigated for unstabilized and stabilized composites. In the first 120h, the elastic modulus increased approximately 11% due to the photo-degradation of LDPE matrix for unstabilized composites. After 120 h UV exposure, elastic modulus was observed to increase continuously with the further UV weathering up to 240 h. This behavior of CF/LDPE was not expected. The strain at break for unstabilzied composites decreased upon increasing UV exposure time. The CF/LDPE composite shows the largest drop than the stabilized composites in strain at break which is nearly 20%. Stabilized with especially HALS (0.5%) showed the best UV additive to protect the tensile strength property of CF/LDPE composites and also retarded the degradation of composites against the UV radiation. The tensile strength of CF/LDPE/UVA (0.2%) composite decreased approximately 21% during the 120h UV weathering. However, no significant reduction observed after 120h. Adding UVA with both ration into the CF/LDPE composites causes the increment to the modulus of elasticity during 120h of weathering, as we expected. The CF/LDPE stabilized composites with UVA (0.2 and 0.4%) also experienced a drop in MOE

Between 120h and 240h of weathering. The photostabilizer UVA (0.4%) clearly prevented some loss in MOE of the CF/LDPE composites after weathering. It can be seen that using antioxidant and UV absorbant effected the tensile properties of composites approximately 10-12% and 12-14%, respectively. However, the stabilized samples did not show the same trend in modulus of elasticity and strain at break properties. Also, the presence of UV additives in the composite structure reduced significantly the rate of decline of the impact strength.

2. Carbonyl index was calculated to investigate the photo-degradation of composites upon UV weathering. The results showed that the carbonyl index for unstabilized composite was the highest value after 240h of exposure. For stabilized composites, UVA offers the important protection to the CF/LDPE composites. Also, the CF/LDPE composites stabilized with HALS was more effective than the other stabilized composites.

3. The crystallinity values were calculated from DSC curves. Chain scission of polyethylene matrix during photodegradation was observed by the crystallinity values of composites. After 120h of weathering, the crystallinity value of unstabilized composites increased due to the chain scission of polyethylene matrix. This value started to decrease after 240h of exposure for unstabilized composites. After 240h of exposure, stabilized composites behaved different from the unstabilized composites. The net change in crystallinity for stabilized composites was not significant. HALS and AOx showed the best results for CF/LDPE composites upon UV weathering.

4. Color measurement of CF/LDPE composites were determined. The Δb* value of CF/LDPE composite which indicates the yellowing of samples decreased significantly after 240h of exposure. The addition of UV absorbers to the composites resulted in retention of photobleaching. The lightness factor ΔL* increased for all composites after 240h of exposure. After 240h of exposure, most of the stabilized CF/LDPE composites ΔL* values are lower than the unstabilized composite. The CF/LDPE composites stabilized with AOx were most effective for lightness (ΔL*) property. The total discoloration (ΔE*) of CF/LDPE/HALS had the highest ΔE* value along the stabilized composites.

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